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Effect of geochemical processes and environment on the spatial pattern of selenium in soil, surface water, and groundwater at the Hovland Ranch, central South Dakota

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EFFECT OF GEOCHEMICAL PROCESSES AND ENVIRONMENT ON THE SPATIAL PATTERN OF SELENIUM IN SOIL, SURFACE WATER, AND GROUNDWATER AT THE HOVLAND RANCH, CENTRAL SOUTH DAKOTA

By

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This thesis meets the standards for appearance, conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

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ABSTRACT

The objective of this paper is to test and review some of the published hypotheses as they may relate to selenium geochemistry in the soil and water system at the Hovland Ranch, Haakon County, South Dakota. Representative samples were collected from soil, water, and soil moisture in the field. Preparation of samples and chemical analysis were done in the Water Quality Laboratory, Dept. of Geology and Geological Engineering, University of North Dakota and Human Nutrition Research Center Lab, USDA/ARS, Grand Forks, North Dakota. The analysis results were statistically analyzed to find correlation between the occurrence of selenium and other associated chemical elements in the soil and water system in the ranch area.

Both total and water soluble selenium in the soil and water samples is significantly positively correlated to sodium, sulfate, sulfur, and phosphorus. Water soluble selenium is mostly selenate. Selenite is below detection limit in the water soluble extracts of soils. Very little total selenium is water soluble, with an average of only 2 %. Selenium is significantly positively correlated to arsenic in both water soluble and acid extracted soil extraction and soil moisture samples. Total organic carbon maintains a positive correlation with selenium. Selenium in the water and soil moisture samples is positively correlated to electrical conductance. Nitrate-nitrogen shows positive correlation with selenium in soil extracts, but the correlation is negative for water and soil moisture samples. Calcium has very little or no correlation with selenium in both the soil (water soluble extracts) and water samples. But calcium has positive correlation with

selenium in the acid extracted soil samples. Total selenium maintains no correlation with depth. Water soluble selenium shows poor but significant negative correlation with depth. Water soluble selenium shows poor but significant positive correlation with elevation. Total selenium has very little spatial variation over the area with insignificant standard deviation, but the spatial distribution of water soluble selenium is distinct with high standard deviation.

All the chemical analysis data suggest that sodium, magnesium and sulfate minerals create a major geochemical sink for water soluble selenium. The solubility of these salts may be the principal factor controlling the mobility and transport of selenium in the soil-water environment.

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Introduction

Scientists and researchers put special interests on selenium research because of the environmental consequences of its double-edged behavior. Selenium, an essential element, also is fatally toxic to humans, livestock, and waterfowl, depending on the amount and chemical form present in the environment. For this reason, there are efforts to seek effective techniques to augment the amount of selenium in selenium deficient lands (Frankenberger et al., 1994). At the same time researchers are concerned with identifying plants and soils with dangerous levels of selenium to protect multiple receptors from acute contamination (Jacobs, 1989). Most early reports focused on selenium toxicity problems (Rosenfeld and Beath, 1964; Lakin, 1972; Oldfield, 1972; etc.). Later reports indicate that selenium is also an essential element in animal nutrition and recently it has been established that it has some beneficial effect on certain types of cancers, especially prostrate cancers (Clark et al., 1996; Finley, 2000; Davies et al, 1999; etc.).

Beginning in the 1930s, a large research effort was begun to identify the sources and distribution of selenium and the mechanisms by which it accumulates in plants and animals (Jacobs, 1989). Special attention was paid to selenium in the environment in the early 1980s, when dramatic evidence of selenium toxicity in the irrigation-induced subsurface and shallow underground waters at San Joaquin Valley in California was

known (Deveral et al., 1984). This incidence triggered a new wave of multidisciplinary research on selenium by wildlife biologists, toxicologists, geologists, microbiologists, agronomists, chemists, and chemical engineers. Due to the concerns expressed by the U.S. Congress, the U.S. Department of the Interior (DOI) started a program in October 1985 to identify the nature and extent of irrigation-induced water quality problems that might exist in the Western United States. The DOI developed a management strategy and formed an interbureau group known as the "Task Group of Irrigation Drainage" that prepared a comprehensive plan for reviewing irrigation-drainage concerns. The Task Group initially identified 20 areas in 13 states and conducted reconnaissance investigations in 9 areas in 1986-87 and 4 areas in 1990-91. On the basis of the results of these investigations, a total of 7 detailed investigations were carried out in 1988-1991 (Rinella et al., 1994). All investigations were conducted by interbureau study teams composed of scientists from USGS, USFWS, BoR, BIA, etc. The investigations are directed toward determining whether irrigation drainage has caused or has the potential to cause significant harmful effects on human health, fish, and wildlife, or may adversely affect the suitability of water for other beneficial use (Frank, 1994). All of these research projects provided much information to understand the complex chemical nature and behavior of selenium in different environments.

1.2 Objectives

The research reported here is a small part of the multi-phase USDA-ARS research project titled "High-Selenium Meat, Wheat and Broccoli: A Marketable Asset?". One of the main objectives of the main research is to evaluate the process of selenium accumulation in foods (wheat, beef, and broccoli) including soil characteristics, plant association, seasonal variation, adsorption, metabolism, and tissue retention. This part of the research is aimed to characterize soil in relation to selenium accumulation and distribution in soils and plants. This research is done with funding from the United States Department of Agriculture/Agricultural Research Service-Grand Forks Research Center.

The major objective of part of the research reported here is to assess the geochemistry of soil, surface water, and groundwater and to characterize the distribution and mobilization of selenium with respect to other chemical constituents (major cations and anions, trace elements, organic matter, etc). A second objective is to correlate the distribution of selenium to the differing rates of plant selenium accumulation over the research area. This particular research does not include the second objective.

The work presented here focuses on an area of known elevated selenium at the Hovland Ranch in Central South Dakota. The goal of the work is to confirm the published hypotheses regarding the relationship between selenium and other chemical constituents. The summary of the main objectives follows:

1. Determine the concentration of selenium (both water soluble and total) and major cations and anions in the soil, surface water, groundwater, and soil moisture samples in the study area. For this purpose, representative samples (soil, surface water, seep, soil

moisture, and groundwater) are collected from surface water and at different intervals in soil horizons, lake bottoms, and groundwater.

2. Run three different soil extraction methods to determine both water soluble and total selenium in the soil samples.

3. Characterize the soils, water, and soil moisture samples in terms of their selenium concentration, major ion chemistry, trace element concentration, physical properties and spatial distribution in the research area.

4. Test the published hypotheses related to selenium geochemistry for the research area.

5. Draw conclusions on geochemical concentrations and association of selenium in relationship to other chemical elements.

CHAPTER 2

DESCRIPTION OF THE STUDY AREA

2.1 Location

The study site at Hovland Ranch lies in the Haakon County, west central South Dakota (Figure 1). The latitude and longitude of the ranch area are approximately 44°25' to 44°27' and 101°2[illegible] to 101°33', respectively. The Hovland ranch is about 5000 acres.

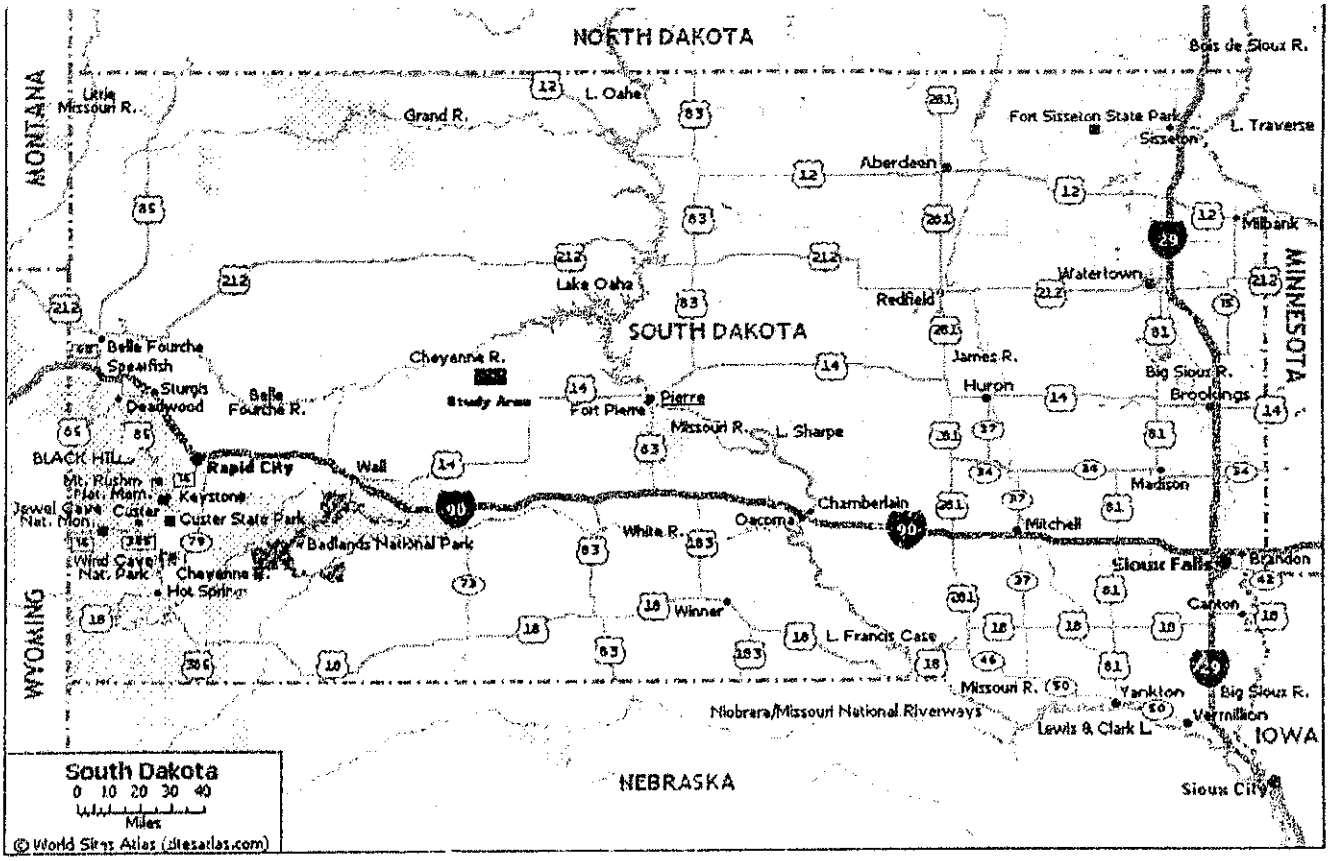


Figure 1. Location of the study area (black rectangle).

2.2 Topography

The Hovland Ranch lies within the Pierre Hills region in the Missouri Plateau section of the Great Plains physiographic division. The topography of the research area varies from open flat grasslands to small flat-topped hills with steep banked stream bottoms. The ranch is drained by intermittent north flowing tributaries to the Cheyenne River and flows throughout the year. The southern part of the ranch is drained by the Bad River and its tributaries and flows during the spring snow melt and after periods of significant rainfall (United States Department of Agriculture, Natural Resources Conservation Service, Soil Survey of Haakon County, South Dakota, 1991).

2.3 Climate

During the winter season, the average temperature is 22 degrees F and the average daily minimum temperature is 9 degrees F. During the summer season, the average temperature is 72 degrees F and the average daily maximum temperature is 87 degrees F. The total annual precipitation is nearly 16 inches. 80% of the precipitation falls in April through September and the growing season for most of the crops are within this period. The average snowfall is about 27 inches. The average relative humidity in mid afternoon is about 50% (United States Department of Agriculture, Natural Resources Conservation Service, Soil Survey of Haakon County, South Dakota, 1991).

2.4 Geology and Superficial Deposits

The geological distribution of selenium gained attention during early recognition of the selenium problem. It long has been known that selenium poisoning or "alkali disease" of livestock in South Dakota is associated with soils derived from Pierre Shale (Franke et al., 1937). Regional geology of the ranch area shows scattered deposits of

Pleistocene gravel, Cretaceous age Pierre Shale, and isolated outcrops of Fox Hills Formation on the surface (Steece, 1961). At the ranch, bedrock consists of Pierre Shale and soils developed thereon (Figure 2).

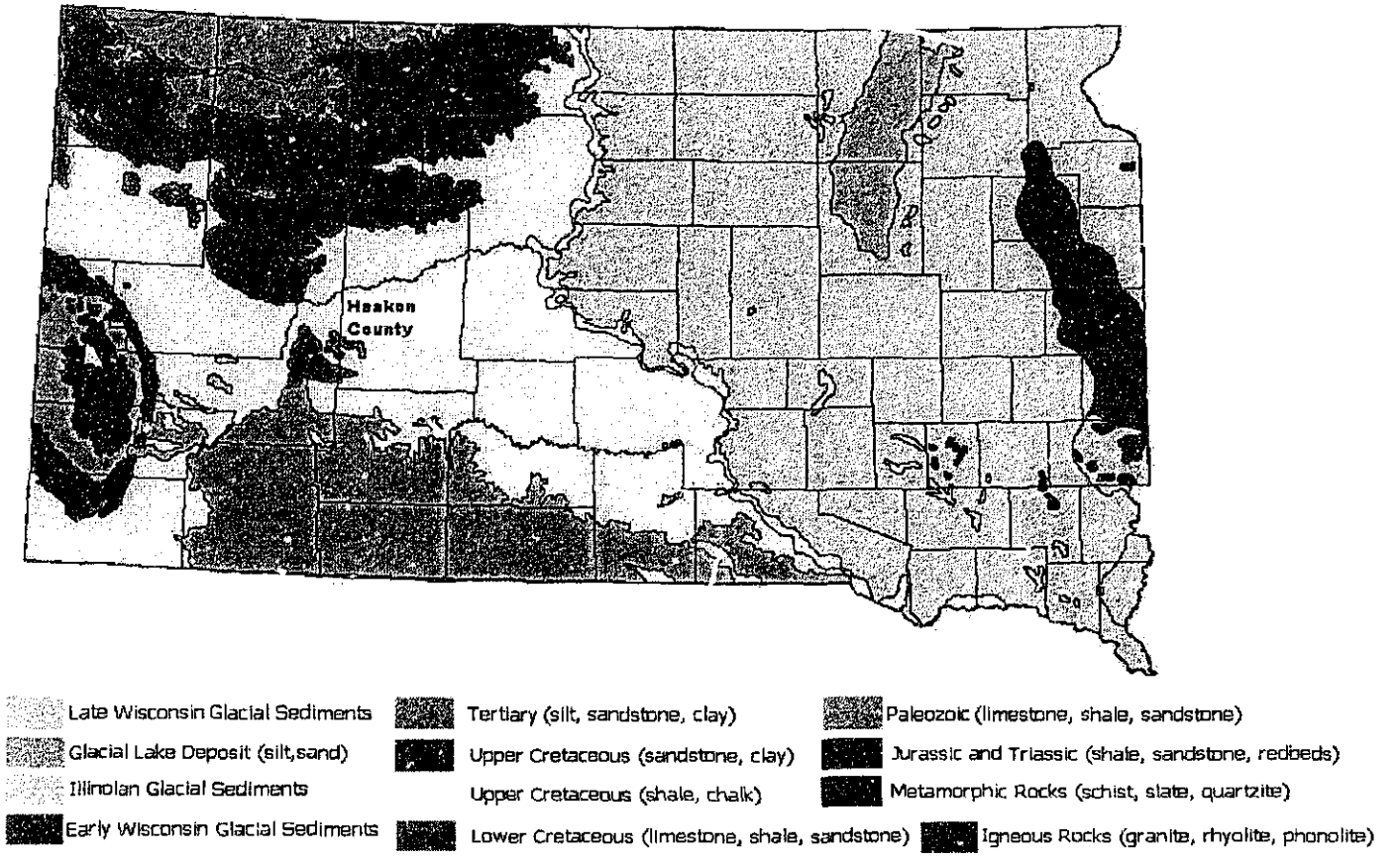


Figure 2. General Geology of South Dakota (USGS, 1951)

2.5 Soil Type

Two major soil associations (Figure 3) cover the research area (United States Department of Agriculture, Natural Resources Conservation Service, Soil Survey of Haakon County, South Dakota, 1991).

Otumwa-Lakoma-Kolls Association

Otumwa-Lakoma-Kolls Association covers the eastern half of the ranch area with some at the middle of the ranch. This association is characterized by low ridges, basins,

and entrenched drainage ways. The soil texture is described by the particle size as clay, silt, silty clay, etc. The Ottumwa and Lakoma soils formed in clayey shale residuum, and the Kolls soils formed in clayey alluvium.

The very deep, well drained Ottuwma soils are on the lower back slopes and on foot slopes. Typically, the surface layer is dark grayish brown silty clay. The subsoil is dark grayish brown, grayish brown, and light brownish gray, calcareous clay and silty clay. It has masses of gypsum and other salts in the lower part. The underlying material is light brownish gray, calcareous silty clay that has masses of gypsum and other salts. The moderately deep, well drained Lakoma soils are on back slopes. Typically, the surface layer is dark grayish brown, calcareous silty clay. The subsoil and the underlying material are grayish brown and light brownish gray, calcareous silty clay. Light gray, calcareous shale bedrock is at a depth of about 28 inches.

The very deep, poorly drained Kolls soils are in basins. Typically, the surface layer is gray clay. The subsoil is gray, calcareous clay. The underlying material is grayish brown and gray, calcareous clay that has masses of gypsum and other salts.

Samsil-Pierre Association

Samsil-Pierre Association comprises the western part of the ranch area with a partial coverage in the middle. This soil association is on breaks along the Cheyenne and Bad Rivers and their tributaries. It is characterized by deeply entrenched drainage ways. The soils formed in clayey shale residuum. This association is composed of 65% Samsil soil, 20% Pierre soils, and 15% minor soils. The shallow Samsil soils are on the shoulder slopes and the upper back slopes. The surface layer is grayish brown, calcareous clay. Below is a transitional layer of grayish brown, calcareous clay. The underlying

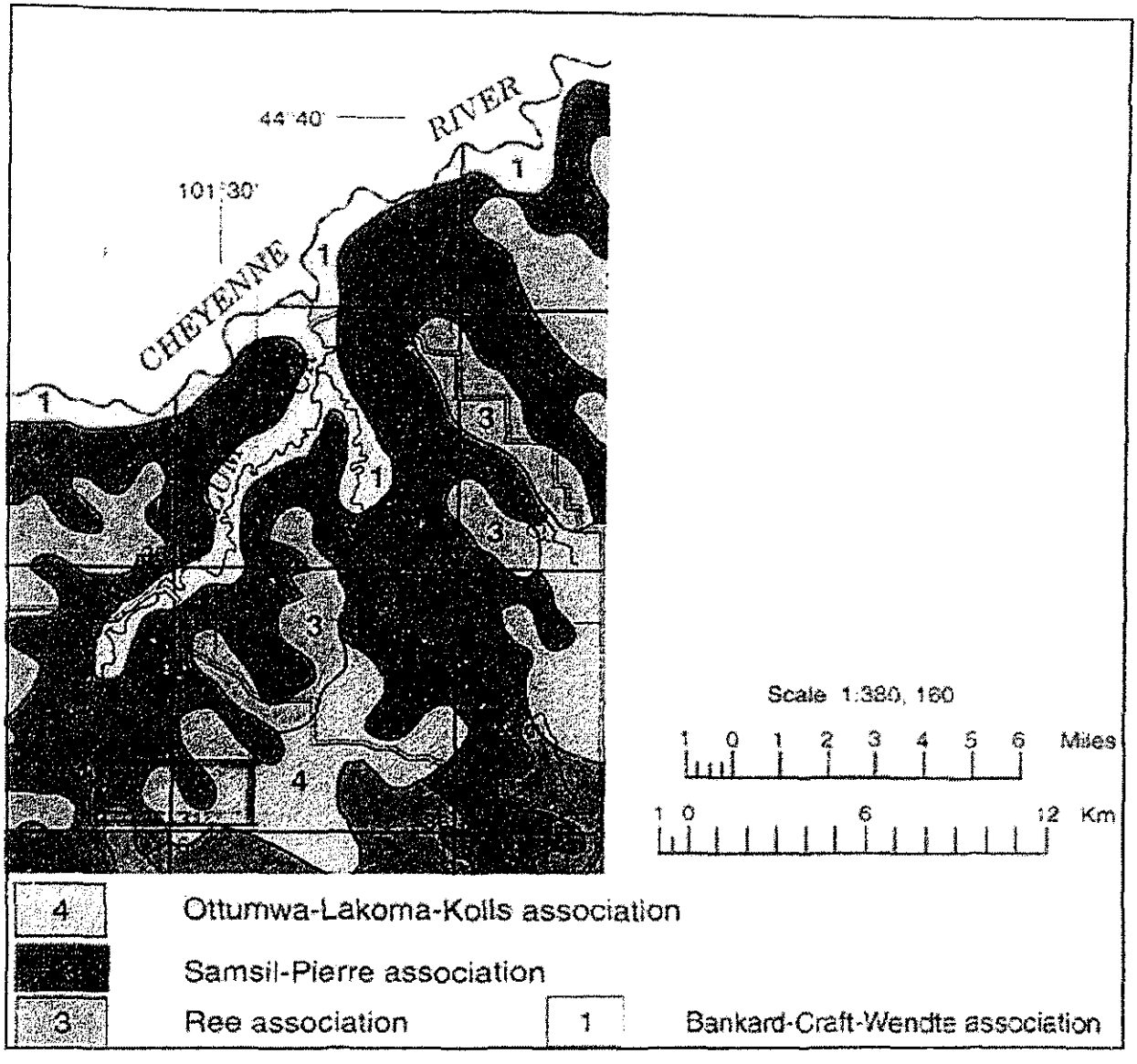


Figure 3. Soil map of the ranch area. The rectangle area in the map is ranch area (United States Department of Agriculture, Natural Resources Conservation Service, Soil Survey of Haakon County, South Dakota, 1991).

material is light brownish gray, calcareous clay. The moderately deep Pierre soils are on the back slopes. The surface layer is dark grayish brown, calcareous clay. Below is a transitional layer of light brownish gray, calcareous clay. It has masses of gypsum in the lower part. Nearly all of this association supports native grasses and is used as range.

2.6 Landuse

Ranching is the principal landuse type in the area. Beef cattle and sheep are the main types of livestock. About 65% of the acreage is range and about 31% is used for cultivated crops or for tame pasture and hay. Winter wheat, grain sorghum, forage sorghum, spring wheat, oat, and alfalfa are the main crops in the area (United States Department of Agriculture, Natural Resources Conservation Service, Soil Survey of Haakon County, South Dakota, 1991).

CHAPTER 3

LITERATURE REVIEW

3.1 Selenium Chemistry

The element selenium belongs to group VI A of the periodic table and was discovered by Jacob Berzelius in 1817. Selenium has chemical and physical properties that are intermediate between those of metals and nonmetals in the VIA group. Other elements which are members of the same group are oxygen, sulfur, tellurium, and polonium. The physico-chemical properties of selenium are summarized in Appendix A. Pure selenium is allotropic and exists as gray hexagonal, red monoclinic, and vitreous amorphous forms. It has a valence of 2- in combination with hydrogen or metals (hydrides and metal selenides), and in oxygen compounds it exists in the +4 (selenite) and +6 (selenate) oxidation states (Jacobs, 1989).

The chemistry of selenium is closely related to sulfur. The concentration, speciation, and association of selenium in an environment depends on the pH and redox conditions, the solubility of its salts, the complexing ability of soluble and solid ligands, biological interactions, and reaction kinetics (Jacobs, 1989). The redox conditions in combination with the pH help control what species of selenium will be present. The redox speciation of selenium is described (Figure 4) in an aqueous system as a function of pH and Eh conditions (Neal et al., 1987). The shaded area of the diagram (Figure 4) indicates the ranges of pH and Eh values for typical soil environments (Neal et al., 1987).

A very short description of selenium species in terms of each oxidation state and in terms of the Eh-pH diagram follows.

Selenide (Se^{2-})

Selenide occurs in reducing environments as hydrogen selenide (H_2Se) and metal selenides (CaSe, Ag_2Se, PbSe, CdSe, etc.), commonly associated with metal sulfide ores. Hydrogen selenide is a weak acid when dissolved in water and easily oxidizes to elemental selenium. Metal selenides are usually found in metal sulfide ores (e.g., Fe, Cu, Pb, etc.), because the ionic radius of Se^{2-} is 0.191nm and that of S^{2-} is 0.184 nm (Weast, 1985) and substitution of Se^{2-} for S^{2-} commonly occurs. Metal selenides, like Se-sulfides, are very insoluble (Elrashidi et al., 1987). Microbial activities can produce volatile methylated derivatives of Se such as dimethyl diselenide (Chau et al., 1976) or dissolved organic selenide compounds (Cutter, 1982; Cutter and Bruland, 1984).

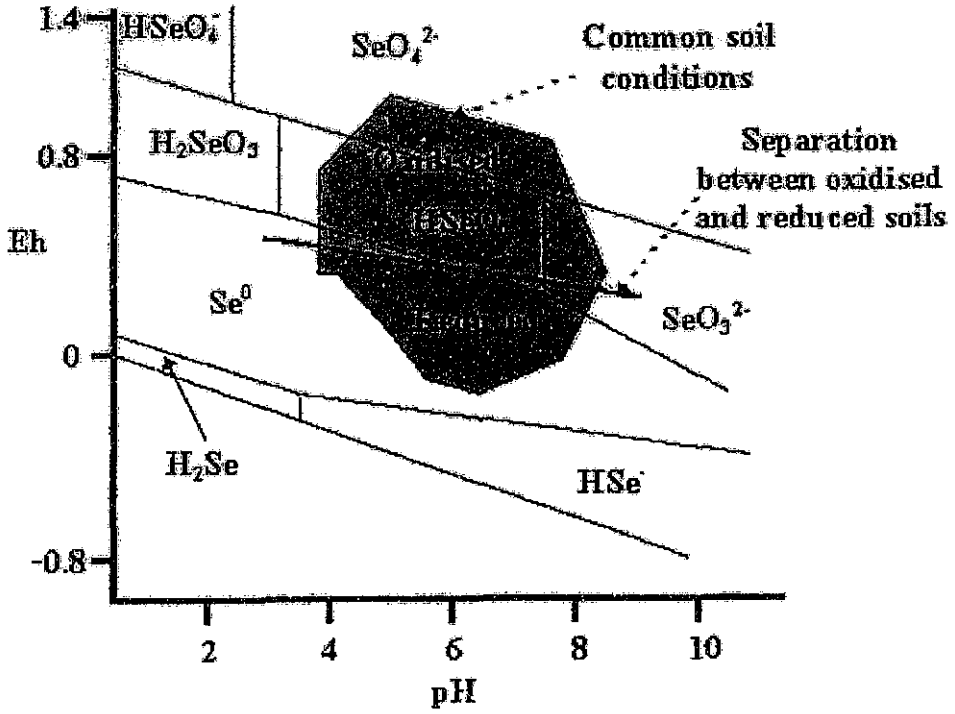


Figure 4. Eh -pH diagram for the system Se-H_2O under the condition Se^T = 1 mmol m^{-3} (Neal et al., 1987).

Elemental Selenium (Se^0)

Elemental Se is stable in reducing conditions. The crystalline forms of elemental selenium (alpha monoclinic and beta monoclinic) are referred to as red crystalline Se. Two amorphous forms of elemental Se are the red amorphous Se of glassy and black varieties (Vokal-Borek, 1979). All these elemental forms of Se are very insoluble in water and the oxidation or reduction kinetics of the solids is very sluggish. Elemental Se can be oxidized to selenite (SeO_3^{2-}) and trace amounts of selenate (SeO_4^{2-}) by certain microorganisms (Sarathchandra and Watkinson, 1981).

Selenite (SeO_3^{2-})

Selenite (4+ oxidation states) occurs in mildly oxidizing conditions. Selenous acid (H_2SeO_3) is a weak acid and is protonated when pH values are acidic to neutral. Most selenite salts are less soluble than the corresponding selenate salts (Elrashidi et al., 1987). Selenite is readily reduced to elemental selenium either by mildly reducing agents or sulfur dioxide in acidic environments (Sarquis and Mickey, 1980) or by microorganisms (Vokal-Borek, 1979). Selenite has a stronger affinity for sorption than selenate. Adsorption of selenite is a function of pH, particle concentration and composition, selenate concentration, and the concentration of competing anions such as phosphate and sulphate (Brown and Carter, 1969; Cary and Gissel-Nielsen, 1973; Balistrieri and Chao, 1987; Ryden et al., 1987).

Selenate (SeO_4^{2-})

Selenate (6+ oxidation states) is stable in well-oxidized environments. Selenic acid (H_2SeO_4) is a strong acid and, therefore, not protonated over the pH range of natural waters. Selenate salts are very soluble (Elrashidi et al., 1987) and selenate is not as

strongly adsorbed as selenite by soil constituents (Merrill et al., 1986; Balistrieri and Chao, 1987). The conversion of selenate to less mobile forms of selenium (selenite or elemental selenium) is a slow process (Sarquis and Mickey, 1980). Of all the forms of selenium, selenate is most readily taken up by plants (Gissel-Nielsen and Bisbjerg, 1970; Eisler, 1985).

3.2 Geomicrobiology of Selenium

Some inorganic forms of selenium are known to be oxidizable by microorganisms. *Micrococcus selenicus* isolated from mud (Breed et al., 1957), a rod-shaped bacterium isolated from soil (Lipman and Waksman, 1923), and a purple bacterium (Sapozhnikov, 1937) have been reported to oxidize Se^{o} to SeO_4^{2-}. A strain of *Bacillus megaterium* from top soil in a river alluvium was found to oxidize Se^{o} to SeO_3^{2-} and traces of SeO_4^{2-}. Red selenium was more readily attacked than gray selenium (Sarathchandra and Watkinson, 1981). *Thiobacilus ferrooxidans* has been reported to oxidize copper selenide to cupric copper and elemental selenium (Torma and Habashi, 1972).

Various inorganic forms of selenium are also reported to be reduced anaerobically by microorganisms. Crude cell extract of *Micrococcus lactilyticus* has been shown to reduce selenite but not selenate to Se^{o}, and Se^{o} to HSe^{-}. All these cases the reductant was hydrogen. Cell extracts from strains of *D. desulfuricans* and *C. pasteurianum* were also found to reduce selenite with hydrogen. The enzyme hydrogenase mediated electron transfer from hydrogen in these reactions (Woodfolk, and Whiteley, 1962). A variety of other known bacteria, actinomycetes, and fungi have been shown to reduce selenate to selenite to elemental selenium (Bautista and Alexander, 1972; Lortie et al., 1992;

Zalokar, 1953). The bacteria include *Pseudomonas stutzeri*, *Wolinella succinogenes*, and *Micrococcus sp. Thiobacillus ferrooxidans* is able to reduce Se^{o} (red form) to H_2Se anaerobically, albeit in small quantities (Bacon and Ingledew, 1989). The oxidizing and reducing capacity of microbes create a cycle (Figure 5) which plays an important role in the distribution of organic and inorganic selenium in soil-water environment.

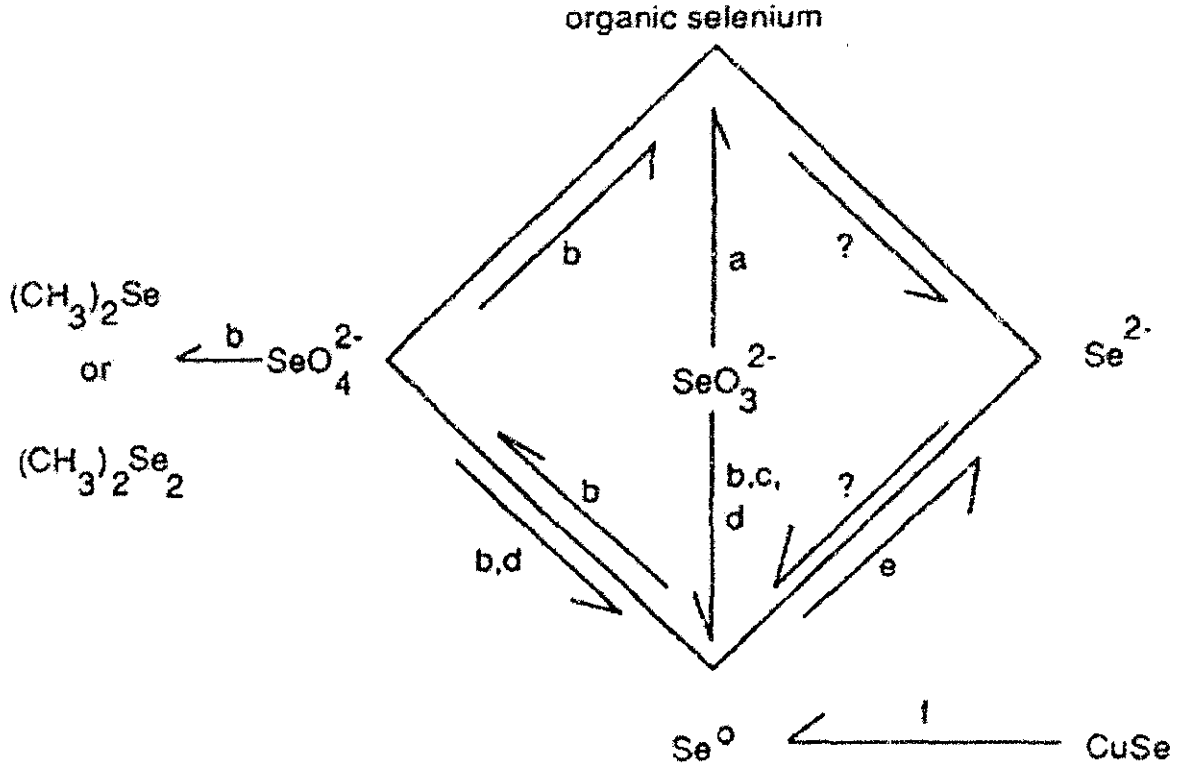


Figure 5. The selenium cycle related to microbes. (a) *E. coli*; (b) bacteria; (c) actinomycetes; (d) fungi; (e) *M. lactilyticus*; (f) *T. ferrooxidans* [Enrlich, 1996].

3.3 Distribution of Selenium in the Environment

Rocks and Soils

The major processes controlling the distribution of selenium are volcanic activity, weathering, groundwater transport, precipitation of minerals, adsorption onto minerals, chemical and biological reduction and oxidation, metabolic uptake and release by organisms, and the burning of fossil fuels (Bauer, 1997; Keller, 2000).

Two types of rocks are usually seleniferous. The first is sedimentary rock of the Carboniferous, Triassic, Jurassic, Cretaceous and Tertiary Age. Sedimentary rocks cover more than three-quarters of the land surface of the earth and are therefore the principal parent materials of agricultural soils. Shale constitutes an estimated 58% of all sedimentary rocks. Cretaceous shale commonly contains the highest levels of selenium (Presser, et al., 1990). During the Cretaceous, selenium was deposited into the central areas of North America during an interval of enhanced, explosive volcanism adjacent to an extensive epicontinental seaway called the Western Interior Seaway.

The erosion and weathering of seleniferous sedimentary and igneous rock can lead to the mobilization of selenium which can then be absorbed and incorporated into other sedimentary rocks, particularly where the sediment is rich in decaying matter (Bauer, 1997).

The second type of rock that has high levels of selenium is sulfide ores of heavy metals (Ag, Cu, Pb, Hg, Ni, etc.). Selenium has been found to replace sulfur in the sulfide crystal lattice by isomorphous substitution of sulfur in minerals. Detailed information about the distribution of selenium in different rocks and soils are presented in the Appendix B.

Selenium enters the soil profile through the weathering and erosion of selenium-rich rocks. Selenium moves through the soil until adsorbed on clay particles, iron hydroxides, or organic particles. Through water and wind erosion and sedimentation processes selenium is distributed and deposited into the soil. Selenium weathered from rocks under alkaline and oxidizing conditions form selenate, which is highly toxic. Selenite and selenate are produced by soil microorganisms from less soluble forms of selenium. These forms are highly soluble in alkaline soils, thus facilitating uptake of selenium by certain plants. Rainy regions are less likely to exhibit elevated concentrations of naturally occurring selenium because selenium and other salts have been flushed from the soil profile. A generalized selenium cycling (Figure 6) can show the path ways of its distribution in the rock-soil-water-plants media. Selenium does not occur in sedimentary rocks from the pre-Cretaceous period such as those in the northeastern U.S., or in the coastal regions where the soils are formed by coastal deposits or recent volcanic ash. There are also low-selenium areas in Montana and Idaho, where the soil is formed from granites and old metamorphic rock; and areas in Arizona and New Mexico where the soil is formed from Tertiary volcanic rock (Ullrey, 1981). Selenium-deficiency disorders such as white muscle disease tend to occur in these areas. Nationwide selenium deficiency in livestock is a far more common occurrence than toxicity. Typically selenium is added to livestock feed as a supplement because the element is lacking in the locally grown forage. So, the distribution of selenium (Figure 7) in the vegetation is an important factor in agriculture and livestock business, as well as in human health.

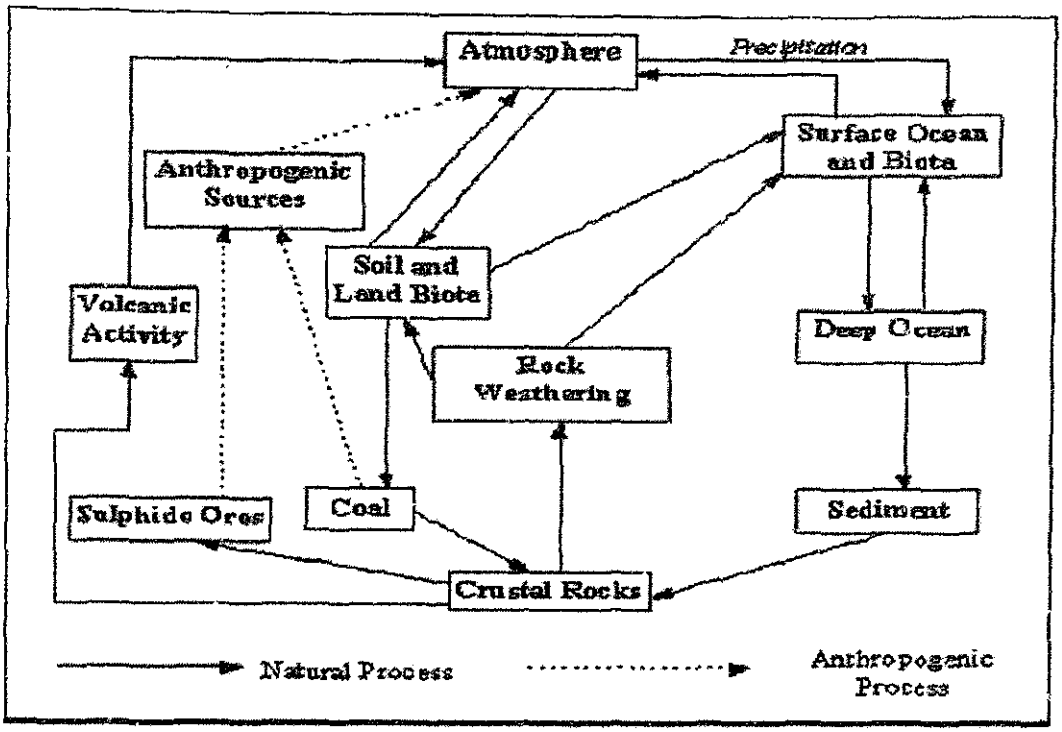


Figure 6. Generalized cycling of selenium distribution within the earth's crust (Herring, 1991).

Fresh Water Systems

In fresh water systems, dissolved selenium usually occurs in three oxidation states: +6, +4, and -2. Turner et al. (1981) reported that when selenium is present as Se (IV) in fresh water at 25 degree Celsius and 1 atm pressure, it exists as selenite ($HSeO_3^-$ at pH 6 and at pH 9 as 31% $HSeO_3^-$ and 69% SeO_3^-) and when present as Se(VI) is found in fresh waters of pH 6-9 as selenate, SeO_4^{2-}. Cutter (1982) noted that selenium in the Se^{2-} oxidation state, selenide ($H_2Se + HSe^-$) or as organic selenides, mainly selenoamino acids bound in soluble peptides, in both oxic and anoxic waters. An overview of selenium concentration and speciation reported in different literature are shown in Appendix C. The selenium concentration in the fresh water systems is directly

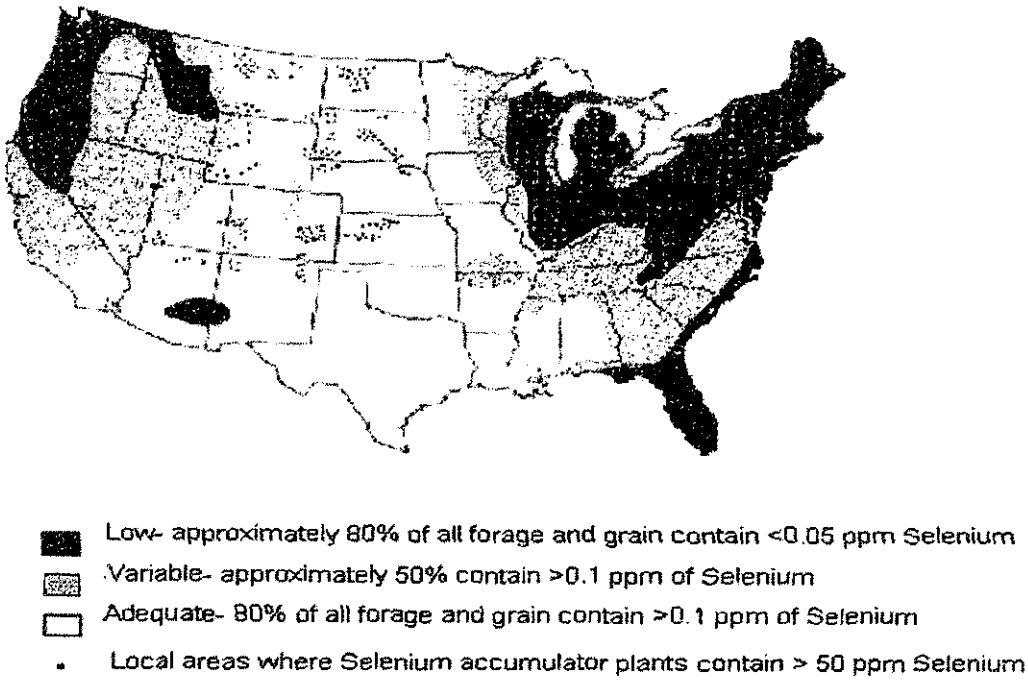


Figure 7. Selenium distribution in vegetation in USA (Kubota et al., 1967).

related to the local geology, weathering of seleniferous sediments, precipitation and runoff, and leaching of soil solutions, and most importantly Eh-pH conditions in both the soil system and fresh water systems.

3.4 Factors Governing Selenium Concentration in Soils

Soil Texture and Mineralogy

Because of the large ionic radius (1.84 Å) selenium does not have the ability to replace a medium-sized cation (0.4-0.8 Å) such as Fe, Mg or Al in the mineral lattice of clay minerals. Clay minerals are well known for their adsorptive qualities in relation to cations, but selenium is most likely to be found in the form of selenite and selenate, which are anions. It would thus be expected that the selenium ions would not easily adsorb onto clays because of repulsion between the two negative fields. Selenium

adsorption onto clay minerals usually occurs at the edges of clay particles (Bar-Yosef and Meek, 1987) as proposed for other oxyanions by Sposito (1984). Bisbjerg and Gissel-Nielson (1969) observed a negative correlation between the clay content of soil and the selenium (regardless of selenate or selenite) concentration in plants. Gissel-Nielsen (1971) also observed that selenite is strongly adsorbed by clays compared to selenate. Hamdy and Gissel-Nielsen (1977) proved that clays and ferric oxide have the capacity to quickly remove selenite from solution, and thus making selenium less available to the plants. They also found that 1:1 clays had a greater selenite fixation capacity than the 2:1 clays as it tends to have a much greater fraction of its total surface area in the form of broken edges. These edges can adsorb H^+ and OH^- and so develop an amphoteric pH-dependent charge (Gast,1977).

Ferric oxide had the highest selenite adsorbed capacity of all the minerals tested. Bisbjerg and Gissel-Nielson (1971) observed that selenium concentrations were as much as two times greater in plants grown in the sandy textured soils compared to plants grown in the loamy-textured soils for both selenium sources. As with the hydrous oxides, a number of factors can influence the extent of selenite and selenate adsorption onto clay minerals. It has been shown that pH is an important factor in selenite/selenate adsorption onto clay minerals (Table 1).

Competing ions can also have a dramatic effect on the adsorption of selenium onto clay minerals. As with the hydrous oxides, PO_4^{3-} is extremely effective in desorbing selenium from mineral surfaces (Table 2).

Table 1. The effect of pH on selenite and selenate adsorption onto clay minerals.

Authors	Media	Species	Low pH	High pH
Hamdy and Gissel-Nielsen, 1977	Kaolinite, montmorillonite and vermiculite	Selenite	Adsorption highest at pH 3	Increasing pH leads to desorption
Frost and Griffin, 1977	Kaolinite and montmorillonite	Selenite	Adsorption highest at pH 2-3	Increasing pH leads to desorption
Bar-Yosef, 1987		Selenite, selenate	Adsorption increased with a drop in pH from 5.6 to 3.6	Increasing pH leads to desorption.
Bar-Yosef and Meek, 1987	Kaolinite and montmorillonite	Selenite, selenate	Adsorption highest at low pH	Increasing pH leads to desorption
Goldberg and Glaubig, 1988	Kaolinite and montmorillonite	Selenite	Adsorption highest at pH 5	Increased pH leads to desorption

Organic Matter

Organic matter can remove selenium from solution in a different way from that of clay minerals (Jacobs, 1989). Levesque (1974) proposed that organometallic complexes may provide important selenium-adsorbing sites. Bisbjerg and Gissel-Nielson (1969) observed that selenium uptake by certain plants were significantly less in organic matter-rich soils than organic matter-poor soils. Singh et al. (1981) reported that the adsorption of selenite and selenate was higher in a soil with elevated levels of organic carbon (0.9%) than from a similar soil with lower levels of organic carbon (0.4%). On the contrary, Davis and Watkinson (1966) proposed that organic matter content of soil increases selenium (selenite) uptake of certain plants.

Table 2. Summary of the effects of various cations and anions on selenite and selenate adsorption.

Authors	Media	Species	Cation/anion added	Results
Bar-Yosef and Meek, 1987	Kaolinite	Selenite, selenate	Phosphate, sulfate	Adsorption reduced by both species
Goldberg and Glaubig, 1988	Montmorillonitic soil	Selenite	Arsenate	Adsorption decreases at pH 9
Rajan and Whatkinson, 1976	Allophane clay	Selenite	Phosphate	Desorption occurs

Competitive Ions

Several competitive ions such as sulfate and phosphate can influence selenium accumulation by plants. Hurd-Karrer (1938) discovered that the addition of either sulfur or gypsum could reduce plant uptake of selenate from soils. Cary and Gissel-Nielsen (1973) showed that the presence of sulfate or nitrate slightly increased the amount of selenate extracted but not selenite. They concluded that sulfate has no effect on the extractability of added selenite from soil. Pratly and McFarlane (1974) showed that increasing the sulfate concentration in soils decreased selenium (selenate) concentration in certain plants. Gissel-Nielsen (1973) observed the same antagonistic effects between selenate and sulfate and to a lesser extent with selenite in a soil experiment. The presence of sulfate in the soil generally reduces the concentration of plant selenium either through direct antagonism or may simply reflect a dilution effect of plant selenium due to increased plant growth by sulfur fertilization (Jacobs, 1989).

A series of conflicting results on selenium-phosphate have been found. Most of the researchers, however, found that soil additions of phosphorus increase selenium accumulation. Carter et al. (1972) found that phosphorus fertilization increased selenium accumulation of alfalfa plants. Singh and Malhotra (1976) reported a positive correlation between phosphorus fertilization and selenium uptake in berseem clover (*Tifilium alexandrinum*). According to Carter et al. (1972), phosphate and selenite may react competitively for same fixation sites. This process may displace selenite on some of the sorption sites, making selenium more plant available. On the contrary, many researchers have found a negative relationship between phosphate and selenium uptake of plants. Singh (1979) reported that phosphorus additions reduce both the selenium concentration

and total selenium uptake by raya plants (*Brassica carinata/ Brassica juncia*). Gardiner (1969) reported an increase in selenium deficiency in livestock following increased use of phosphorus fertilizers on soils where animals were grazing in parts of Australia. Mikkelsen et al. (1988) reported a negative correlation between plant selenate uptake and boron and chloride salinity in the irrigation water.

3.5 Plant Uptake of Selenium

Some plants, like *Astragalus spp.* and *Stanleya*, can accumulate large amounts of selenium as organic selenium compounds. Not all forms of selenium in the soil are available for assimilation by these plants. Selenium is required nutritionally as a trace element by few microorganisms, plants and animals, including human beings (Stadtman, 1974). But, still there is debate on the nutritional requirement of selenium to plants and researches are going on this topic. It has been found to be an essential component of the enzyme glutathione peroxidase mammalian red blood corpuscles (Rotruck et al., 1973). When selenium occurs in alkaline soils (such as those of the western U.S.) and becomes oxidized as selenate, the selenium becomes water-soluble. This form is highly toxic and easily leached from the soil and available to plants. In acid soils, whether selenium occurs as a trace element or as selenide (bound to other metals), the selenium is still toxic, but not actively available to plants in higher levels on the food chain.

The concentration of selenium in soils is estimated to be 0.2 ppm (Rosenfeld and Beath, 1964). Acute toxicity in animals occurs when the vegetation eaten contains 10,000 ppm of selenium. Chronic diseases can occur when the ingested food contains from 5-40 ppm of selenium over a sustained period of time. Olson (1978) investigated chronic toxicity in cattle and found that chronic selenosis or "alkali disease" could be produced

by prolonged feeding of inorganic selenium. However, his results could not necessarily be duplicated, suggesting widespread differences in the susceptibility among cattle and other factors in the biological cycle of selenium uptake and absorption that should be further investigated.

Absorption by plants depends on the chemical form and solubility of the selenium as well as the moisture content of the soil. Some plants require selenium to grow and possess a high content of seleniferous materials, e.g., *Astragalus*, *Haplopappus,* and *Xylorrhiza* (Jacobs, 1989). Other plants may not require selenium for growth, but will accumulate the element if grown in seleniferous soils. The first group is known as primary indicator plants because their presence indicates that selenium is actually present in the soil in potentially large amounts. Plants belonging to the second group, such as alfalfa, western wheatgrass, onions and Swiss chard, are called secondary converter plants. While they can grow in selenium-free soils, they can also grow well in seleniferous soils and accumulate concentrated, potentially toxic amounts. The total concentration of selenium in soils does not directly determine the concentration of selenium in the plants growing on those soils (Lakin, 1972). Different factors (Table 3) that control selenium toxicity and selenium deficiency are a combination of complex geochemical processes. The chemical bonding and reaction patterns are the critical determining factors because different chemical forms vary in their solubility and subsequent availability to plants (Anderson and Scarf, 1983).

Table 3. The factors that cause toxic seleniferous soils, non-toxic seleniferous soils, and low selenium soils (National Research Council, 1971)

Se in rocks	Aridness	Soil drainage	Chemical Reaction	Availability of Plants	pH	Toxicity and soil type
High	Subhumid	Well drained/ poorly drained	Selenides and other insolubles converted to selenates and organic selenium compounds	High	Alkaline	Toxic: the higher the acid level, the less selenium will be available to plants
High	Humid	Well drained	Slightly soluble complexes of ferric oxide or hydroxide and silent ions will be formed	Medium	Acid	Non-toxic: sufficient selenium to protect from selenium deficiency
Low	Humid or Dry	Well drained/ poorly drained	Minimal selenium to perform a chemical reaction	High or Low	Alkaline/ acid	Low selenium generally means low toxicity: the higher the Ph and the more humid the area, the greater the chance of selenium deficiency

3.6 Selenium Poisoning and Beneficial Effects

Selenium is an essential trace element or micronutrient in human and animal health. However, too little or too much of it in the diet can lead to ill-health and even death. Selenium is an important component of glutathione peroxidase (GSHPx) and is thought to be a critical enzyme in the body which combats oxidative damage at a cellular level. Selenium deficiency in humans has been associated with a number of diseases. These include cardiovascular disease, cancer, periodontal disease, cystic fibrosis, alcoholic cirrhosis and Legionnaire's disease (Gissel-Nielsen et al., 1984). Large numbers of studies using rats and mice have shown that dietary selenium can have a protective effect against a range of induced tumors (Lavender, 1986).

Acute Toxicity

Acute poisoning is caused by the consumption, usually in a single feeding, of a sufficient quantity of highly seleniferous plants, which produce severe symptoms. Usually, death occurs within a few hours. Cattle and sheep are the most likely species to

be affected, but also horses, goats, and swine. Studies have shown that possibly as little as 3 mg/kg body weight is the minimum lethal dose in cattle, for horses it may be 3.3 mg/kg body weight, and for swine, 1.2 mg/kg body weight caused death in 5 days. There is no known treatment to reverse the effects of the poisoning, and oftentimes the animal dies before a diagnosis can be made.

Chronic Toxicity

There are two different types of chronic poisoning, depending on the chemical form of the ingested selenium. "blind staggers" occurs when animals ingest water-soluble selenium compounds naturally found in accumulator plants. Toxicity from eating plants or grai.. with protein-bound, insoluble selenium is called "alkali disease."
These are some of the *Astragalus* species (Jacobs, 1989) that carry high levels of selenium which have a wide enough range and large enough population to be of concern include *A. bisulcatus, A. pattersonii, A. pectinatus, and A. racemosus.*

These plants usually have a characteristic musky odor due to the volatile dimethyl selenium compounds that they contain, generally causing animals to avoid them. However, under certain conditions, animals will turn to them as a source of food. Selenium toxicity causes two main syndromes: blind staggers and alkali disease. These two syndromes are not necessarily independent of one another. An animal may have only symptoms of one or the other or a combination of the symptoms of both. Both are associated with cardiac and skeletal muscle damage as well as hepatic damage.
Blind Staggers. This syndrome may occur within a brief period (a few days to a few weeks) after the animal has begun to take in very high dietary levels of selenium. The symptoms of this condition are: impaired vision, a depressed appetite, and wandering in

circles. Without removal of the high Se intake, this can progress to varying amounts of paralysis and finally death from respiratory failure.

Alkali Disease. This is a more chronic disease associated with lower level and longer duration intake of selenium. It is characterized by emaciation, loss of hair, deformation and shedding of hooves, loss of vitality and erosion of the joints of long bones.

3.7 Hypothesis Related to Selenium Geochemistry

The following hypotheses related to selenium geochemistry have been identified and published in previous work. The main objective of this research is to test these hypotheses in a known high selenium area at the Hovland Ranch, Haakon County in central South Dakota.

1. High Se concentration is generally associated with high dissolved solid concentrations (Crist, 1974).

2. Se concentration generally increases with depth. Total and water soluble Se concentrations are significantly higher in soils in the 60 to 90cm depth interval as compared to the 0 to 30cm depth intervals (Jacobs, 1989).

3. Organic matter has a large capacity to remove Se from solution and extraction of the high organic matter soil revealed very little soluble Se as compared to the other soils tested (Jacobs, 1989). Se concentration will decrease with increasing organic matter as organic matter with Fe and some metals are the major adsorbing place for Se (Frankenberger and Benson, 1994).

4. Phosphate will increase Se accumulation in soils (Jacobs, 1989). Most investigators have found that soil additions of phosphorus (P) increase selenium accumulation. Carter et al. (1972) proposed two possible mechanisms for selenium-

phosphate interactions: (a) phosphate and selenite may react competitively for sites. When phosphate is added to soils, it may displace selenite on some of the sorption sites, making selenium more plant available.

5. Se commonly occurs in groundwater only if nitrate is present (Weres et al., 1989), because redox conditions that are sufficiently oxidizing to favor nitrate stability also favor selenate stability and because selenate reduction is mediated by microbes that preferentially use nitrate as an electron acceptor over selenate (Oremland et al., 1989).

6. Sodium and magnesium sulfate minerals, containing selenate, act as temporary geologic sinks for selenium (Presser et al., 1990; Frankenbereger et al., 1994). Theoretically, the open lattice structures of these hydrous minerals could incorporate the selenate anion into the sulfate space. If the dissolved selenium comes from dissolution of these evaporative salts, then Se concentration would be expected to increase with the increasing of these elements (sodium, magnesium, and sulfate). Sodium, magnesium, sulfate and selenate were significantly correlated in the soils and sediments in the San Joaquin Valley of California.

7. Gypsum precipitation has some control on Se mobility. In comparison with sodium and magnesium sulfate salts, gypsum does not seem to tolerate the substitution of selenate for sulfate places (Presser et al., 1990).

CHAPTER 4

METHODOLOGY

Representative water, soil moisture, and soil samples were collected from the ranch area in the year 2001 and 2002 (Figure 8 and Figure 9). Samples from different media (water, soil moisture, and soil) were collected to find the variability of chemical elements with respect to selenium concentration and to understand the selenium geochemistry in each media. These samples were preserved and prepared for chemical analysis. Data sets from the chemical analyses were used to test different published hypotheses related to selenium geochemistry and to decipher the natural processes that modify the spatial and vertical distribution of selenium at the Hovland Ranch study site. Sample locations were collected by using GARMIN GPS (coordinates of UTM Zone 14 with WGS 1984 datum).

4.1 Field Sampling and Field Measurement

Water and Soil Moisture Sampling

Seven water samples were collected from seven locations. Three were from ponds, two from boring wells, one from natural seep, and one from the ranch stock well. Six soil moisture collection sites were selected in the study area (Figure 8 and Figure 9). At each site two soil moisture collection devices were placed in two depth intervals of 30-40 cm and 50-60 cm respectively. Soil moisture was collected by evacuating air pressure (70-75 centibars of soil suction) from the sampling tube. Collected soil moisture was filtered and preserved for anions, cations, and organic carbon analysis in three

different containers. Samples for cations were preserved after adding 2ml concentrated Nitric acid for 100 ml of samples.

Water samples (Figure 8 and Figure 9) were collected in two separate 250 ml plastic containers. Waters were filtered using 0.45 micron filters. For each sampling location, one water sample was acidified (2ml concentrated HNO_3 for 100 ml of samples) for cation analysis and the other is non-acidified for anion analysis. Sixty ml filtered water samples were collected in amber glass bottles for total inorganic and organic carbon analysis. The acidified water samples were used for selenium analysis.

Field Measurements of physical properties of water and soil moisture, including pH (ORION, Model 290A), EC, temperature, salinity (HACH, Model C0150), and DO (YSI, Model 85/50 FT) were done by using field meters. All the field meters were calibrated at the start of each day of sampling. Checks were then carried out randomly during the day to ensure no drift took place.

Soils Sampling

Ninety-five soil samples (Figure 8 and Figure 9) were obtained from the ranch area. All the soil samples were collected by using hand augers and were preserved in plastic bags.

4.2 Preparation of Soil Samples

Approximately 300 g of each soil sample were placed in a wide mouth glass jar and heated in an oven at a temperature of 30-40°C for approximately three days (until dry). A low oven temperature is used to minimize possible loss of selenium through volatilization. The samples were then disaggregated and ground with a clean pestle and mortar before being sieved through a non-metallic 1 mm mesh.

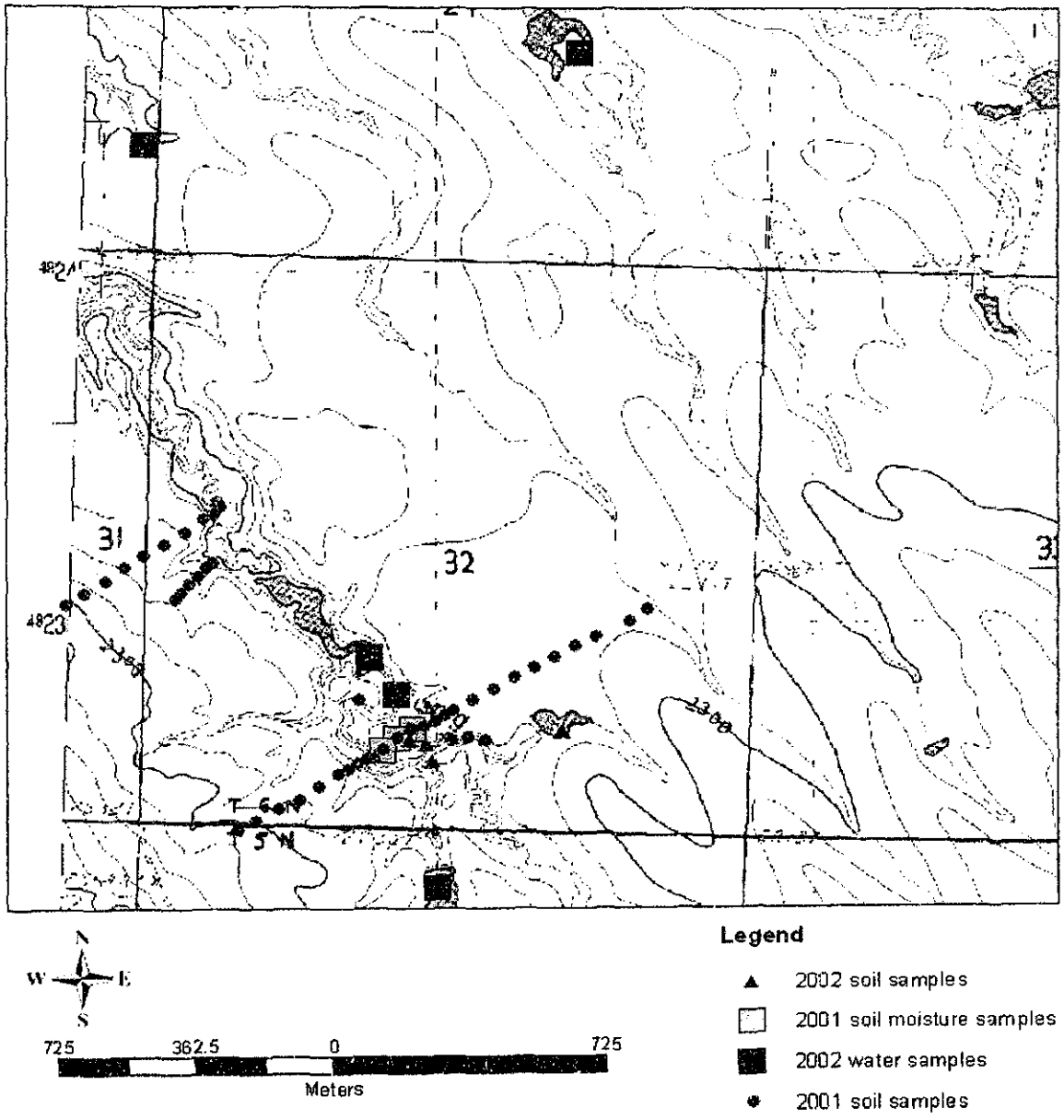


Figure 8. Sampling locations on the eastern side of the Hovland Ranch
Base map is a 7.5 minute series topographic map (Middle Draw, Haakon County, SD) of provisional edition 1983, USGS]

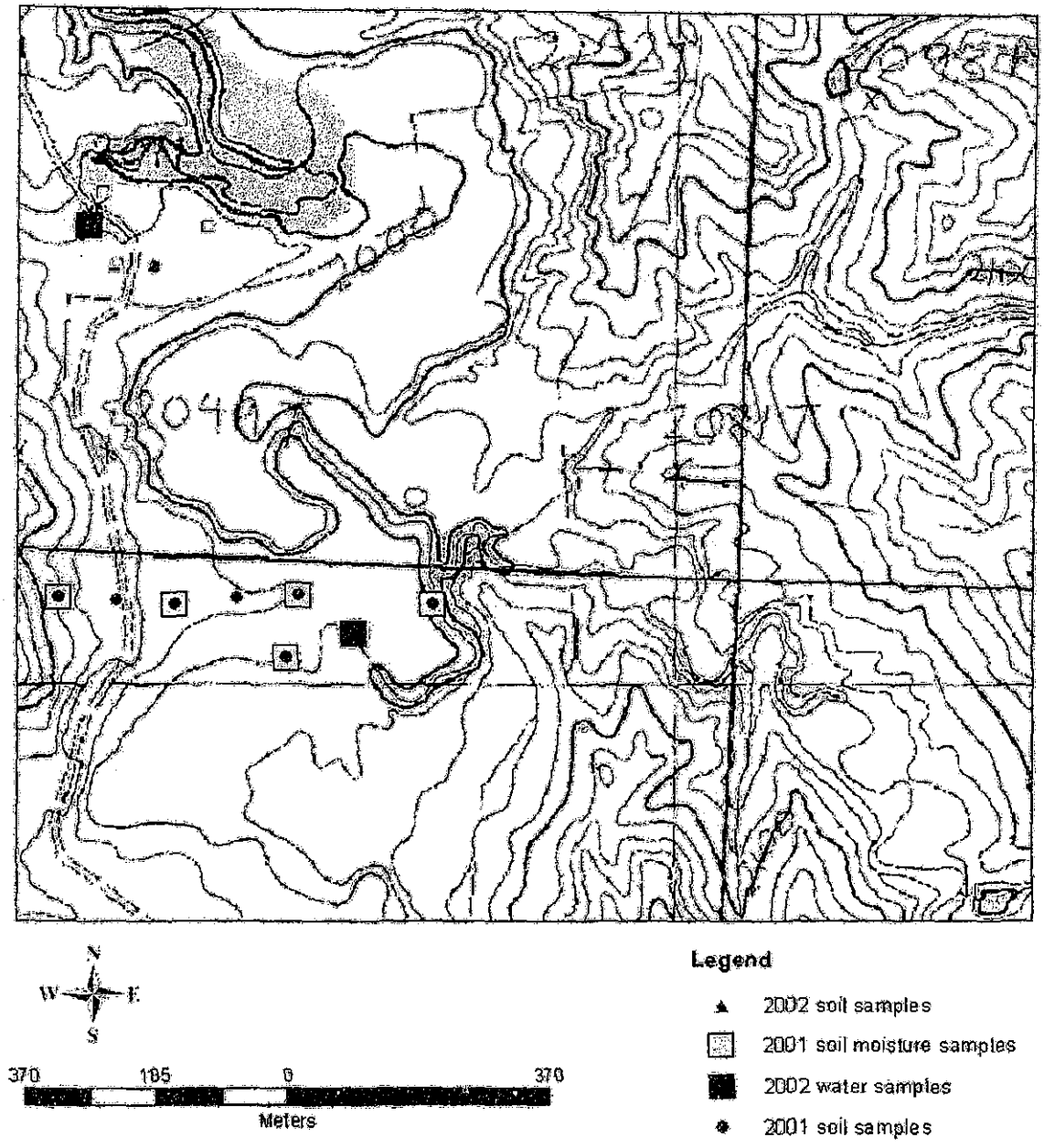


Figure 9. Sampling locations on the western side of the Hovland Ranch.
[Base map is a 7.5 minute series topographic map (Murray Draw, Haakon County, SD) of provisional edition, 1983, USGS]

4.3 Preparation of Soil Extracts form Soil Samples

All the chemical parameters of soil samples were measured from soil extracts. Three types of soil extraction procedures (Appendix D) were used to obtain soil extracts from the collected soil samples:

1. Hot Water Extraction (Neve, 1980) : Used to determine water soluble portion of metals including selenium and arsenic in soils sampled in 2001.
2. Saturated Paste Extraction (Spackman et al., 1994): Used to determine water soluble portion of anions and cations including selenium and arsenic in soils sampled in 2002.
3. Acid Extraction (Hossner, 1996): Used to determine total cations including total selenium and total arsenic in some selected soil samples of 2001 and soil samples collected in 2002.

4.4 Chemical Analysis Techniques

A range of techniques was used to chemically characterize the samples (water samples, soil moisture samples, and soil extracts).

Major Anions. Water samples, soil moisture samples, and soil extracts (2002 Soil Samples) were analyzed for Cl^-, $SO4^{-2}$, NO^{3-} and PO_4^{-3} by using a Dionex DX-120 Ion Chromatograph equipped with AS 50 Auto Sampler. SOP from Dionex DX-120 Ion Chromatograph manual was followed.

Major Cations. For the analysis of major cations and trace elements a Flame Atomic Absorption Spectrophotometer was used. A SOLAAR AA Spectrometer (Thermo Elemental) equipped with flame photometer and FS 95 Furnace Auto Sampler was used. SOP from SOLAAR AA manual was followed.

Organic and Inorganic Carbon. For organic and inorganic carbon in the waters and few selected soil extracts were measured by using a Shimadzu TOC 5000 analyzer. For water and soil moisture samples, Shimadzu's ASI 5000 Auto Sampler was used. For solid soil samples, Shimadzu's Solid Sample Module SSM 5000A was used.

Selenium Analysis by Hydride Generation Atomic Absorption Spectrometry. Selenium is most soluble in its +6 valence (selenate) state. In this study selenium analysis is carried out using the hydride technique which involves formation of the gaseous hydride (SeH_2). However, to measure selenium using the hydride technique the selenium needs to be in the +4 valent state as only this form will react with sodium borohydride (the reductant) to form the gaseous hydride. Therefore, before waters and soil extracts can be analyzed, the selenium present in the waters must be reduced to the +4 (selenite) forms. An acid pretreatment system is practiced to achieve this condition (Spackman et al., 1994). An atomic absorption spectrometer (AAS) in conjunction with the hydride generation technique used to measure the selenium.

Hydride-Generation Atomic Absorption with Flow Injection Sample Introduction. Five ml of the sample aliquot were reduced by adding 3 ml of ARISTAR grade HCl in a polycarbonate tube with screw top and heating in a water-bath for 1 hour at 80 °C.
A 0.5 ml aliquot of the prepared sample is injected into a flowing stream of HCl and the sample is mixed with a flowing stream of $NaBH_4$ (0.2 % w/v) and NaOH (0.05 % w/v). The addition of the $NaBH_4$ and the NaOH reduces the dissolved selenium to gaseous selenium hydride (SeH_2). The combined mixture is then mixed with Ar gas before separating the SeH_2 from the liquid phase in a gas liquid separator. The Ar and the SeH_2 then pass through a Nafion drying tube and into a quartz tube furnace (900°C) mounted in

the light-path of a Perkin Elmer 3100 atomic absorption spectrometer (AAS) running a Perkin Elmer selenium electrode less discharge lamp (EDL). The SeH_2 is thermally decomposed into selenium atoms which absorb light at 196 nm. The selenium concentration is determined by the amount of absorbance measured by the AAS. Selenium +4 standards of 0, 1, 5, 10 and 20 ppb were used to calibrate the AAS before analysis. The standards are made up using serial dilution from a 1000 ppm Spectrosol grade standard solution, in 1 % HCl. In addition, a number of Aquacheck™ samples of known selenium concentrations were also analyzed through the run to check for accuracy. After every 10 samples a blank and a 10 ppb selenium standard are run to check for any drift. If any significant drift did occur then re-calibration would take place. *Graphite Furnace Atomic Absorption Spectrometry.* GFAAS is also used to analyze selenium for the water samples and soils sampled in 2002 to compare the results with the HGAAS.

A SOLAAR AA Spectrometer (Thermo Elemental) equipped with graphite furnace and FS 95 Furnace Auto Sampler is used for selenium analysis. SOP from SOLAAR AA manual was followed. To eliminate the matrix effect nickel nitrate matrix modifier with concentrated nitric acid is used.

4.5 Quality Control and Precision of Chemical Data

Different quality control measures were taken to ensure data quality (Appendix K). For every analysis, standard curves were prepared using analytical grade standards (chemicals). Quality control check samples together with routine preparation blank and duplicate samples were run for each batch of chemical analysis.

4.6 Statistical Analysis

Statistical analysis techniques are used to show the strength of correlation between selenium and other chemical constituents in the chemical analysis data.

Linear Regression Analysis. A simple linear regression model gives a straight-line (least squares regression line) relationship between two variables. The equation of a linear relationship between two variables x and y is written as y= a + bx. Here, "a" is intercept of the regression line at y axis, and "b" is slope which denotes a change in y due to a change of one unit in x.

If "b" is positive (+) it denotes a positive linear relationship between the two variables. If "b" is negative (-), it denotes a negative linear relationship between the two variables.

The detail regression analysis is done by using Excel's (Microsoft Corporation) Regression tool. The analysis determines R^2 (coefficient of determination, which gives the proportion of SST or total sum of squares that is explained by the use of the regression model) and r (linear correlation coefficient, measuring the strength of the linear association between the two plotted variables). Usually, the higher the r, the better the regression model. If r is positive (+), it denotes a positive linear relationship between the two variables. If r is negative (-), it denotes a negative linear relationship between the two variables.

The regression tool also test the significance of correlation between the two variables by using F-test and t-test and the significance of correlation is denoted by significance F or p-value. Usually, the lesser the p-value, the better the correlation between the two variables (for example, p-value of 0.01 means 99% significance, and p-

value of 0.1 means 90% significance, etc). For this research, the level of significant is assumed 90% or more. Correlation below 90% significance level is assumed insignificant.

4.7 Geochemistry of Selenium and Testing of Hypotheses

By using all the chemical analysis data and their interpretation, the geochemistry of selenium with respect to other chemical elements (cations, anions, organic matter, etc.) was outlined. An attempt was made to test several published hypotheses regarding selenium geochemistry by using the trend and results of the chemical analysis of all the soil moisture, water, and soil samples.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Chemical Analysis

2001 Soil Moisture Samples Analysis

Three batches of soil moisture samples were collected from the Hovland Ranch on 01 August of 2001(12 samples), 09 August of 2001(11 samples), and 27 August of 2001 (7 samples).

A total of 12 soil moisture samples were collected from six locations in every sampling batch. Two samples from each location at two different depths of 0.3 m to 0.4 m and 0.5 m to 0.6 m, respectively, were collected. Due to the lack of soil moisture content, not all samples for each sampling location were collected.

These soil moisture samples were analyzed for chloride, nitrate-nitrogen, sulfate, conductivity, total organic carbon, arsenic, mercury, and selenium (Appendix E). The chemical analysis data were statistically analyzed and summarized in Table 4.

Summary of Chemical Analysis of 2001 Soil Moisture Samples. For all the samples both selenium and arsenic concentration are below 3 ppb. The selenium and arsenic concentrations are much below 3ppb as the samples were not adequately acid pretreated for selenium and arsenic analysis. It is supposed that a significant portion of soluble selenium (selenate) is not in the reduced form (selenite). For this reason, a major portion of water soluble selenium is not detected by HGAAS method. No significant variation of

selenium concentration is found in these three phases (collected at different time intervals) of soil moisture samples.

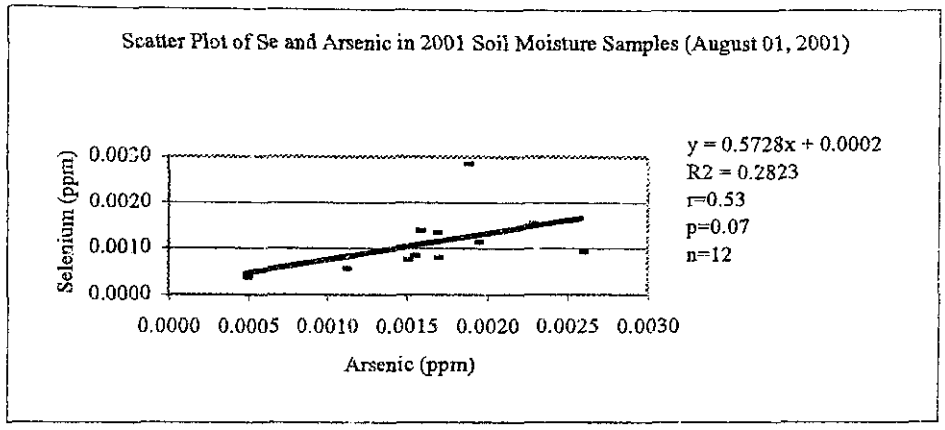
Table 4. Statistical parameters for chemical analysis data of 2001 Soil Moisture Samples

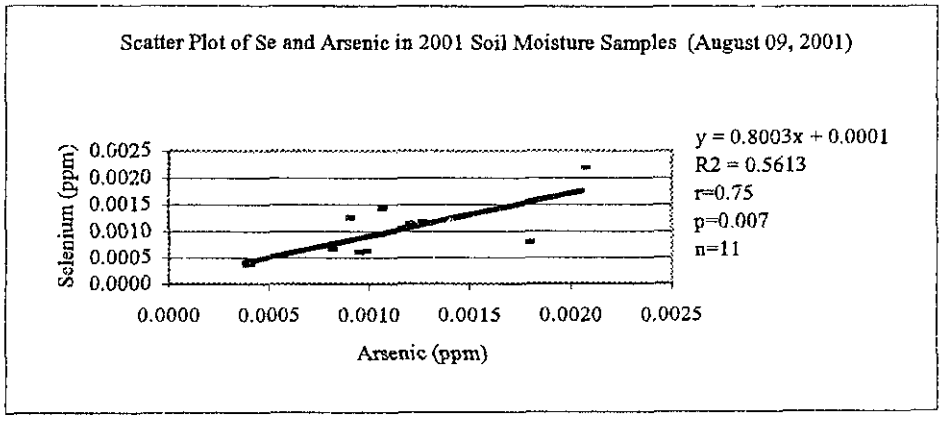
Period	Statistical Parameters	Cl^- (ppm)	NO3-N (ppm)	SO_4^{2-} (ppm)	Cond (mS)	TOC (ppm)	Hg (ppm)	As (ppb)	Se (ppb)
Aug01	Average	60.15	2.92	312.7	2.11	16.73	0.0014	1.55	1.07
(n=12)	Maximum	276	13.2	1820	8.74	58.8	0.0048	2.58	2.85
	Minimum	9.3	<1	19.1	0.79	0.6	0.0001	0.48	0.36
	Std. Dev	78.31	4.25	502.47	2.18	14.84	0.0015	0.63	0.68
	r with respect to Se	0.78	- 0.70	0.86	0.88	0.94	0.57	0.53	
	p-value with respect to Se	0.001	0.03	0.0004	0.0001	0.000007	0.05	0.07	
Aug09	Average	31.46	3.62	176.49	1.53	15.41	0.0053	1.06	0.96
(n=11)	Maximum	133	16.5	533	2.78	36.8	0.0263	2.06	2.19
	Minimum	1	<1	8.4	0.74	<1	0.0004	0.38	0.36
	Std. Dev	40.11	5.95	195.92	0.77	10.55	0.0074	0.51	0.54
	r with respect to Se	0.48	- 0.60	0.26	0.47	0.53	0.34	0.75	
	p-value with respect to Se	0.14	0.1	0.43	0.14	0.09	0.31	0.007	
Aug27	Average	13.86	5.53	259.59	1.16	4.31	0.0020	1.11	0.643
(n=7)	Maximum	28.2	16.2	1280	2.27	12.6	0.0122	2.66	1.34
	Minimum	3.4	<1	31.4	0.76	<1	0 0004	0.38	0.306
	Std. Dev	8.61	7.58	461.28	0.54	4.09	0.0046	0.90	0.340
	r with respect to Se	0.03	ND	0.19	0.37	0.83	ND	0.54	
	p-value with respect to Se	0.95	ND	0.69	0.41	0.04	ND	0.27	

Selenium has significant positive correlation (Figure 10, Figure 11, Figure 12) with arsenic for August 01 (r=0.53, p=0.07) and August 09 (r=0.75, p=0.007) samples, but for August 27 (r=0.54, p=0.27) the correlation is not significant. Selenium has significant positive correlation with TOC for August 01 (r=0.94, p=0.000007), August 09 (r=0.53, p=0.09), and August 27(r=0.83, p=0.04). Selenium has significant positive correlation with conductivity for August 01 (r=0.88, p=0.0001) samples, but the correlation is insignificant for August 09 (r=0.47, p=0.14) and August 27(r=0.37, p=0.41) samples. Selenium has significant positive correlation (Figure 13) with chloride for soil moisture samples of August 01 (r=0.78, p=0.001) But selenium has insignificant correlation with chloride for soil moisture sample of August 09 (r=0.48, p=0.14) and August 27 (r=0.03, p=0.95). Selenium has significant negative correlation (Figure 14) with nitrate-nitrogen (r= - 0.70, p=0.03 for August 01, r= - 0.60, p=0.1 for August 09). Due to lack of samples. regression analysis was not done for selenium with nitrate-nitrogen for soil moisture samples of August 27 (n=3). Selenium has significant positive correlation (Figure 15) with sulfate (r=0.86, p=0.0004 for August 01). But selenium maintains insignificant positive correlation with sulfate for soil moisture sample of August 09 (r=0.26, p=0.43), and August 27 (r=0.19, p=0.69). Selenium has insignificant weak positive correlation or no correlation with depth (r=0.17, p=0.59 for August 01, r=0.24, p=0.48 for August 09, r=0.26, p=0.57 for August 27). The important points of the chemical analysis of soil moisture samples are:

1. In most of the samples selenium has significant positive correlation with arsenic, TOC, and conductivity.
2. Selenium has significant negative correlation with nitrate-nitrogen.

3. No significant correlation with depth.
4. Selenium has significant positive correlation with chloride (except soil moisture sample for August 09 and August 27).
5. Selenium has significant positive correlation with sulfate (except soil moisture sample for August 09 and August 27).





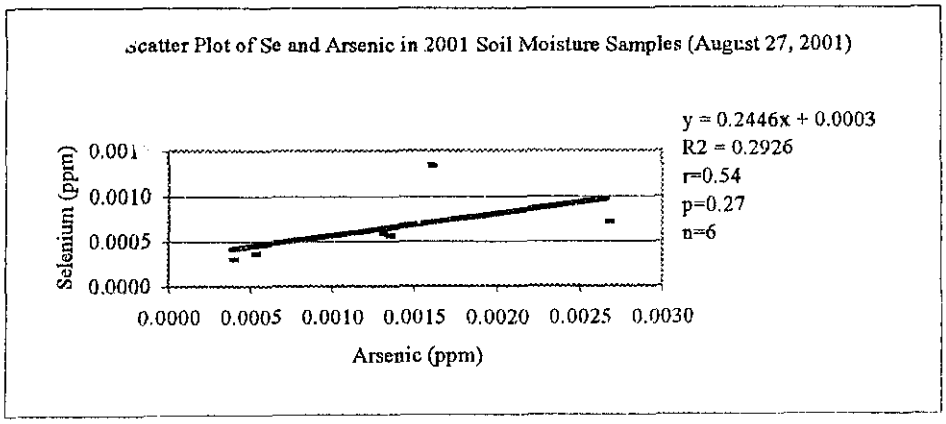
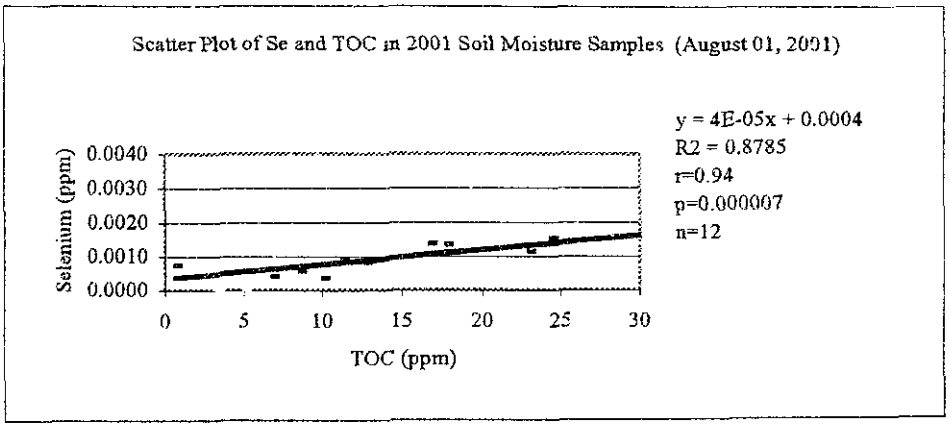
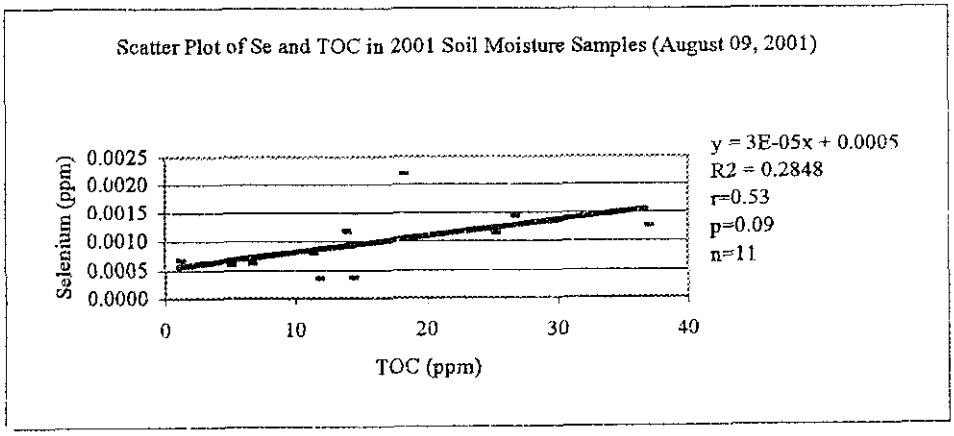


Figure 10. Scatter plot of Se and Arsenic in 2001 Soil Moisture Samples





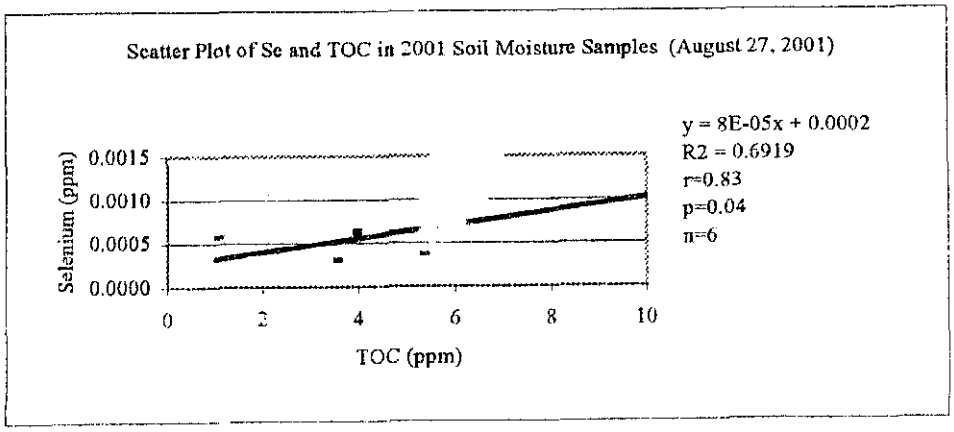
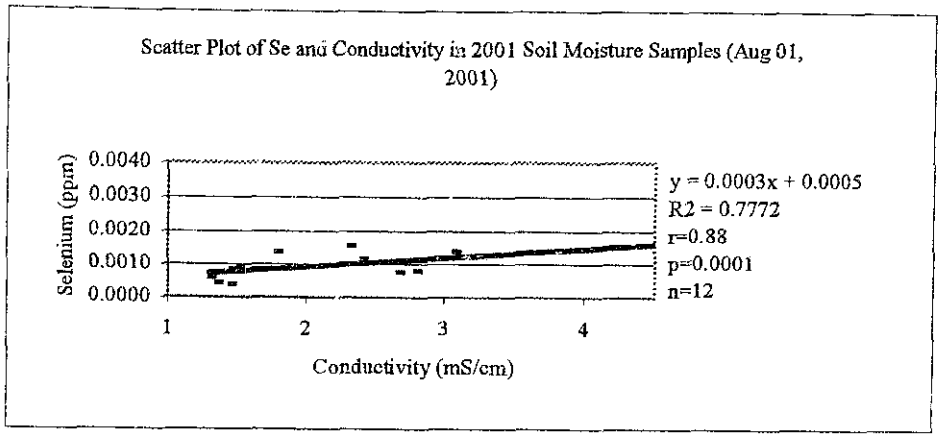
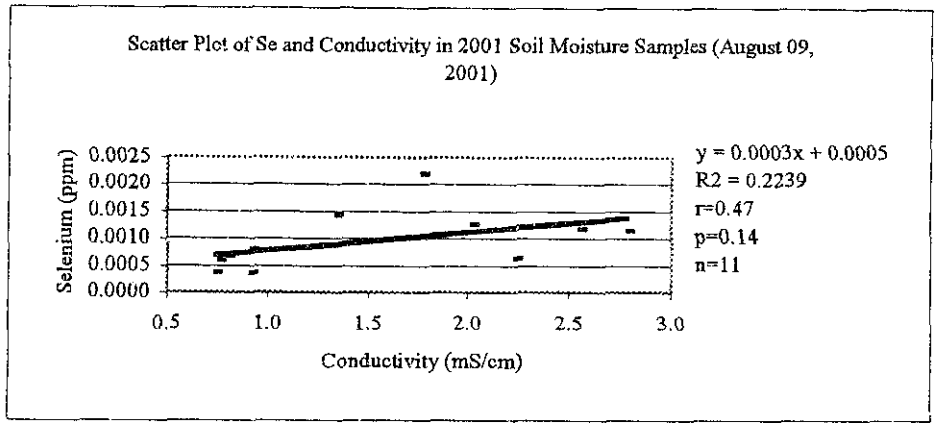


Figure 11. Scatter plot of Se and TOC in 2001 Soil Moisture Samples





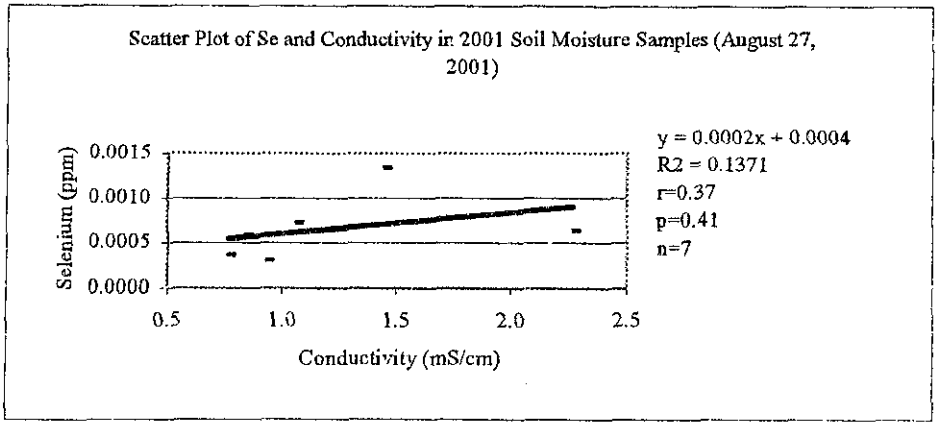
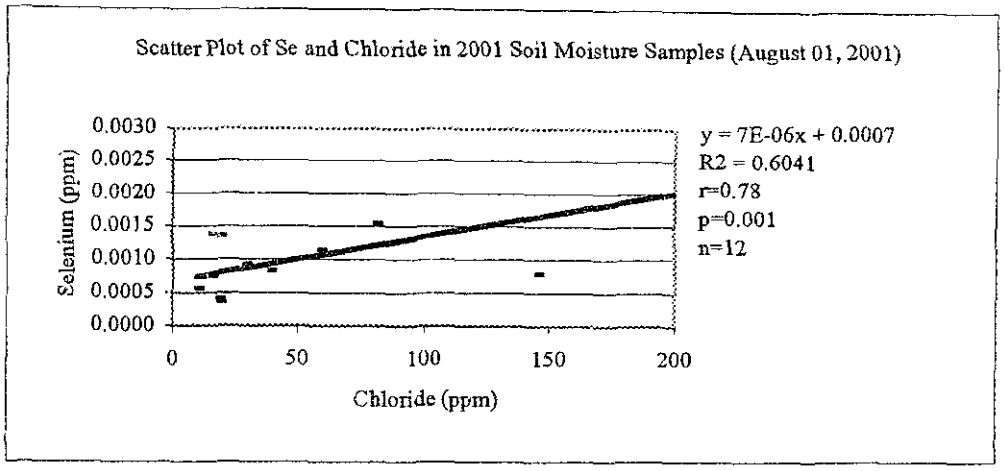
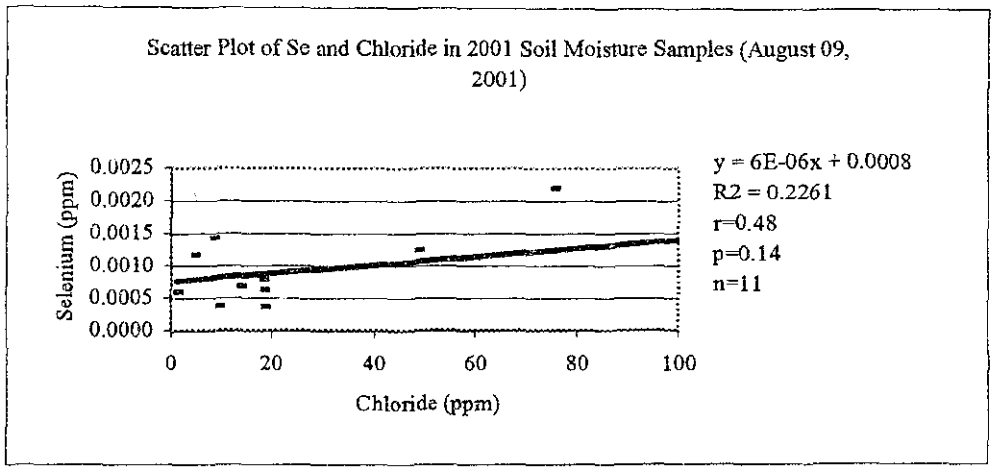


Figure 12. Scatter plot of Se and Conductivity in 2001 Soil Moisture Samples





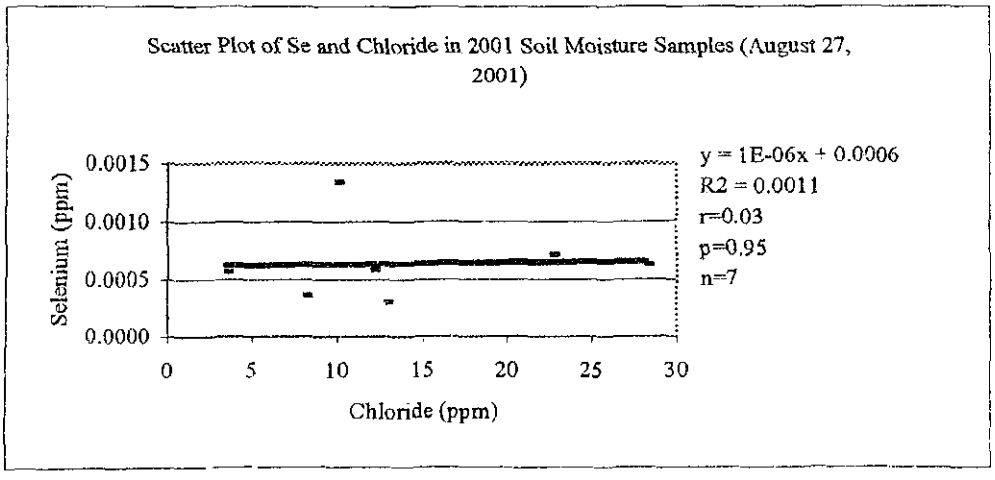
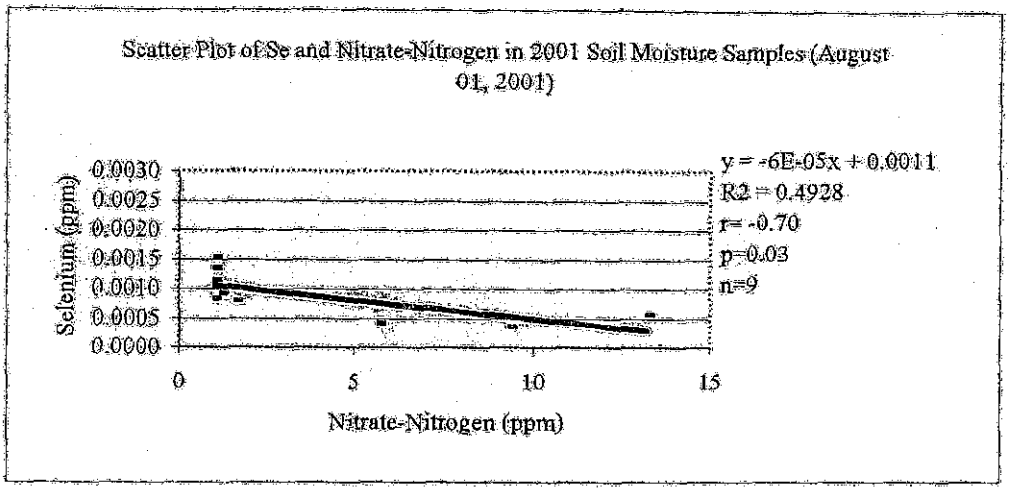


Figure 13. Scatter plot of Se and Chloride in 2001 Soil Moisture Samples



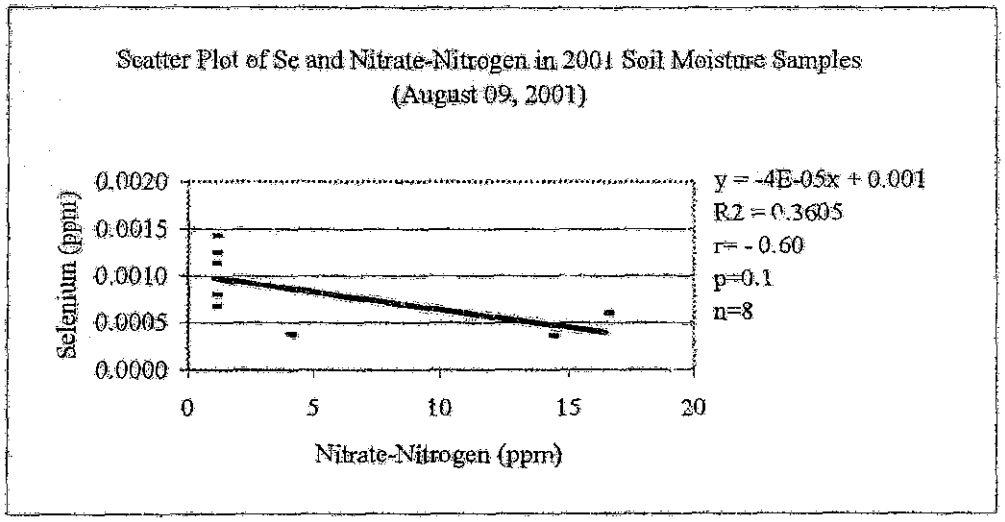
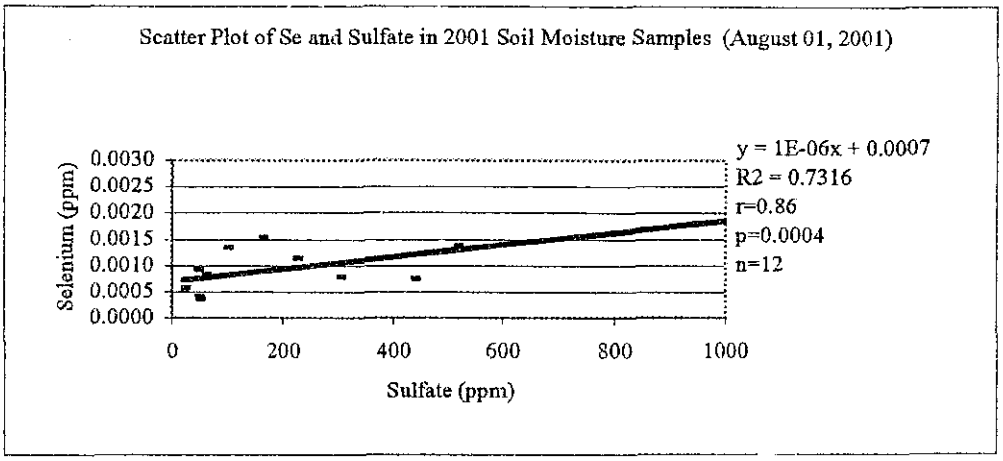
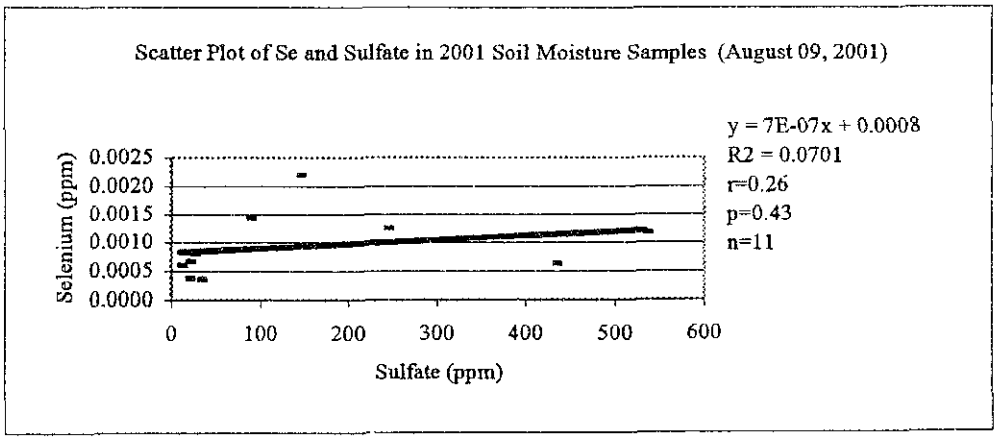


Figure 14. Scatter plot of Se and Nitrate-Nitrogen in 2001 Soil Moisture Samples





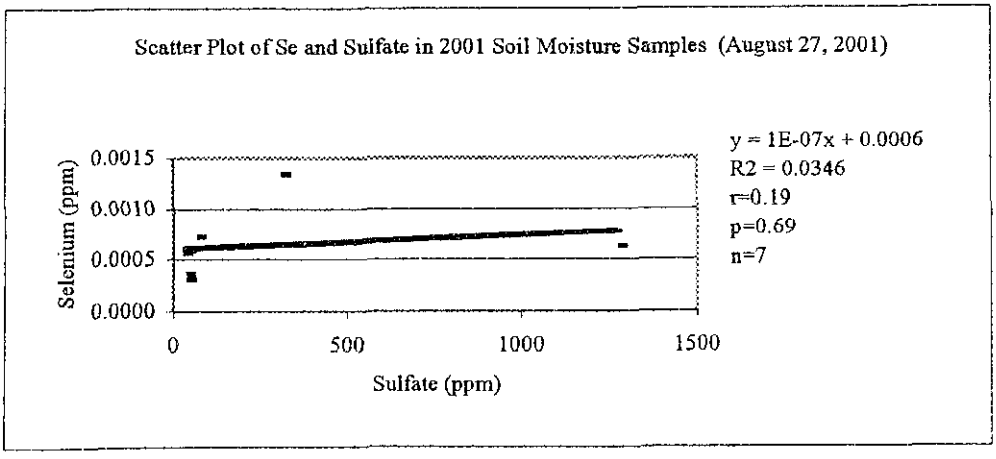


Figure 15. Scatter plot of Se and Sulfate in 2001 Soil Moisture Samples

2002 Water Sample Analysis

Seven water samples were collected from the Hovland Ranch area in August 2002.

1. Four surface water samples from four ponds
2. One natural seep water sample, and
3. Two groundwater samples from two borings

The samples were analyzed for major cations, major anions, TOC, DO, EC, selenium, arsenic, etc. (Appendix F). The chemical analysis results were statistically analyzed and summarized in Table 5. The statistics do not include the chemical analysis results of the seep sample (Sample ID: S1) collected in the northeastern part of the ranch, which is exceptionally high in chemical concentration and different in origin compared to the other water samples.

Summary of Chemical Analysis of 2002 Water Samples. The seep water sample is exceptionally high in chemical elements compared to the other water samples, especially conductivity (10190 µS/cm), chloride (494.97 mg/l), Nitrate-N (165.18 mg/l), sulfate (8607.64 mg/l), Magnesium (900.3 mg/l), sodium (428.4 mg/l), and selenium (4178.68 ppb by GFAAS and 1739.55 ppb by HGAAS). Selenium concentration is below the maximum permissible limit of 10 ppb in all the samples except the seep sample according to the analysis results from HGAAS. According to GFAAS technique, samples from *Astragalus* slope (Sample ID: Astra, Se:10.76 ppb) and ranch well (Sample ID: Ranch, Se :21.15 ppb) are above the maximum permissible limit of 10 ppb.

Table 5. Statistical parameters for chemical analysis data of 2002 Water Samples (n=6).

Parameters	Average	Max	Min	Std. Dev	Linear Correlation Coefficients (r) with Respect to Selenium	Significance F/ p value
Cond. (µS/cm)	3601	5900	1163	2078	0.53	0.27
pH	7.25	7.8	6.7	0.51	0.20	0.70
DO (mg/l)	4.67	5.8	2.6	1.16	0.07	0.90
Cl (mg/l)	46.06	76.80	19.77	22.34	0.63	0.18
NO3-N (mg/l)	23.17	29.04	20.97	3.53	- 0.28	0.60
SO_4^{2-}(mg/l)	4141.98	7243.08	1070.02	2704.02	0.58	0.23
P (mg/l)	0.01	0.04	<0.01	0.02	ND	ND
TC(mg/l)	90.88	186.7	29.18	56.36	ND	ND
IC(mg/l)	71.2	162.2	12.0	59.92	ND	ND
TOC(mg/l)	19.70	42.65	3.5	13.53	0.25	0.63
HCO_3^-(mg/l)	361.7	823.99	60.96	304.38	0.43	0.39
Ca(mg/l)	556.64	1038.69	133.93	331.57	0.02	0.98
Mg (mg/l)	316.03	902.2	87.63	313.0	0.92	0.009
Na (mg/l)	206.59	316.99	102.83	81.39	0.72	0.1
K (mg/l)	20.73	34.16	11.98	7.39	0.87	0.02
Fe (mg/l)	0.05	0.07	0.01	0.02	0.20	0.70
Mn (mg/l)	9.23	55.02	<0.01	22.43	0.13	0.80
S (mg/l)	1025.63	2108.87	274.76	693.45	0.77	0.07
Cu (mg/l)	0.03	0.08	<0.01	0.04	ND	ND
Mo (mg/l)	0.03	0.04	<0.01	0.02	0.48	0.34
Zn (mg/l)	0.01	0.06	<0.01	0.02	ND	ND
Se(ppb)_GF	7.97	21.15	1.17	7.33	0.21	0.69
Se(ppb)_HG	3.23	8.03	1.7	2.37		

Selenium has significant positive correlations (Figure 16, 17, 18) with sodium (r=0.72, p=0.1), magnesium (r=0.92, p=0.009), potassium (r=0.87, p=0.02), sulfur (r=0.77, p=0.07), and TOC (r=0.87, p=0.02). Selenium has insignificant positive correlation with Sulfate (r=0.58, p=0.23), chloride (r=0.63, p=0.18), and conductivity (r=0.53, p=0.27). Selenium maintains an insignificant negative correlation with nitrate-nitrogen (r= -0.28, p=0.60). The scatter plot and regression analysis of selenium and calcium (r=0.02, p=0.98) shows that there is no correlation between them.

Selenium concentration results are different between GFAAS and HGAAS analysis techniques. This difference may be due to the variation of intensity in oxidizing the organic matter and other selenium form and finally to reduce them in selenite form in the two methods of analysis. The important points of chemical analysis of water samples are:

1. High selenium content is significantly positively correlated to high sulfate, sulfur, magnesium, potassium, sodium, and TOC.
2. Selenium has insignificant negative correlation with nitrate- nitrogen.
3. The seep water has the highest selenium content in the area with exceptionally high ionic concentration.
4. High selenium is positively correlated to high electrical conductance (r=0.53, p=0.27).
5. Selenium shows no relationship to calcium.

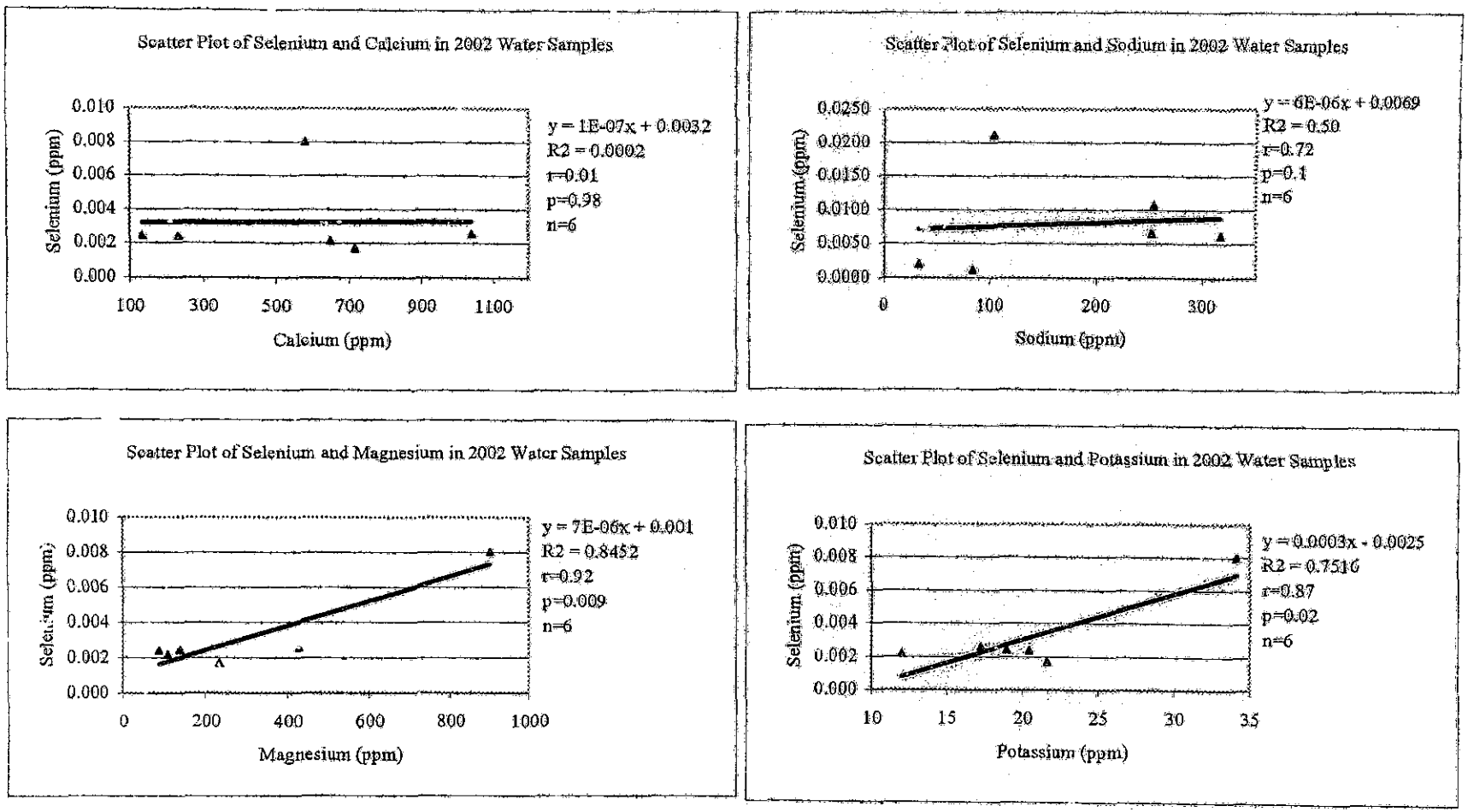


Figure 16. Scatter Plot of Se with Calcium, Sodium, Magnesium, and Potassium in 2002 Water Samples

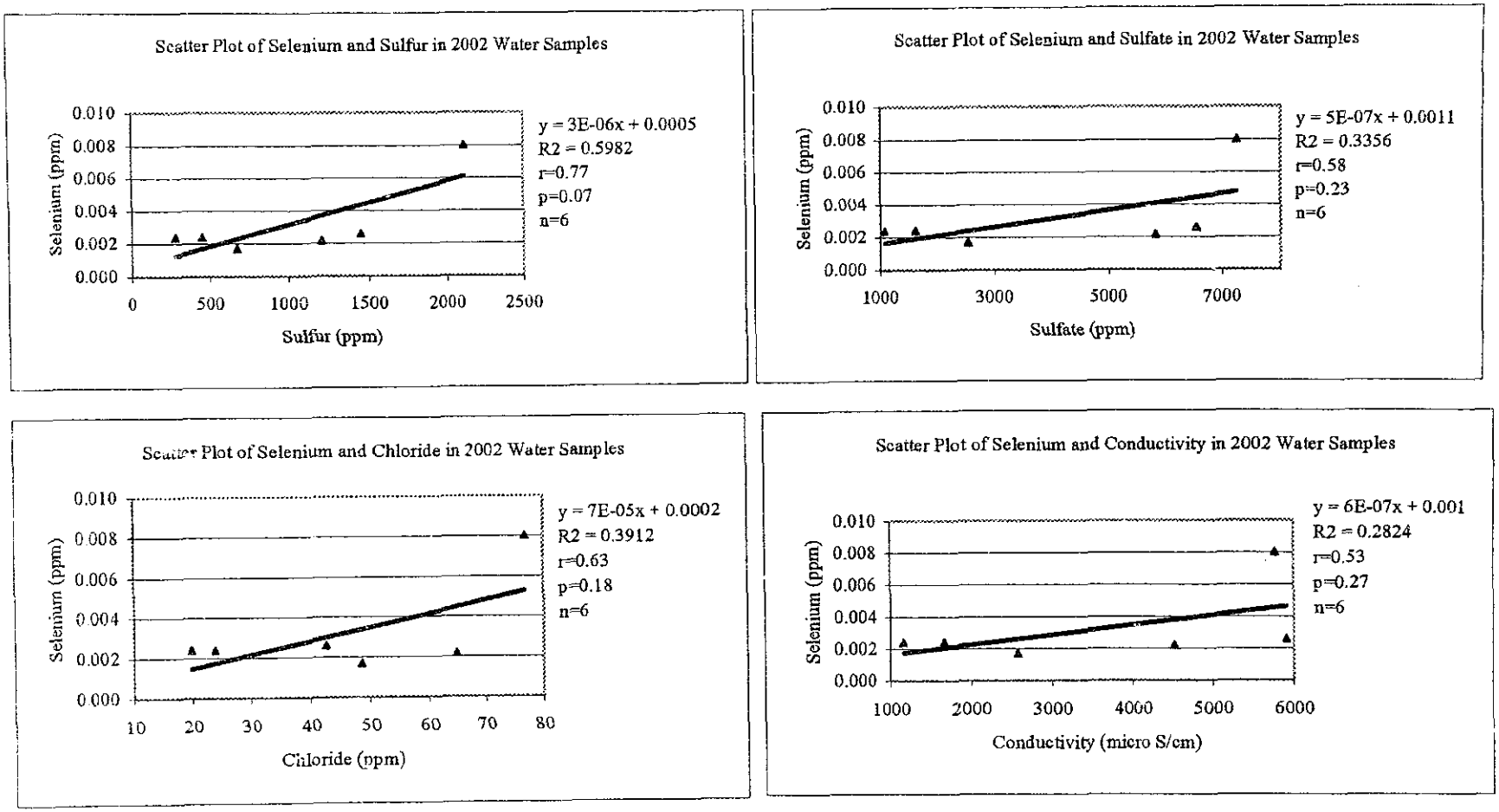


Figure 17. Scatter Plot of Se with Sulfur, Sulfate, Chloride, and Conductivity in 2002 Water Samples

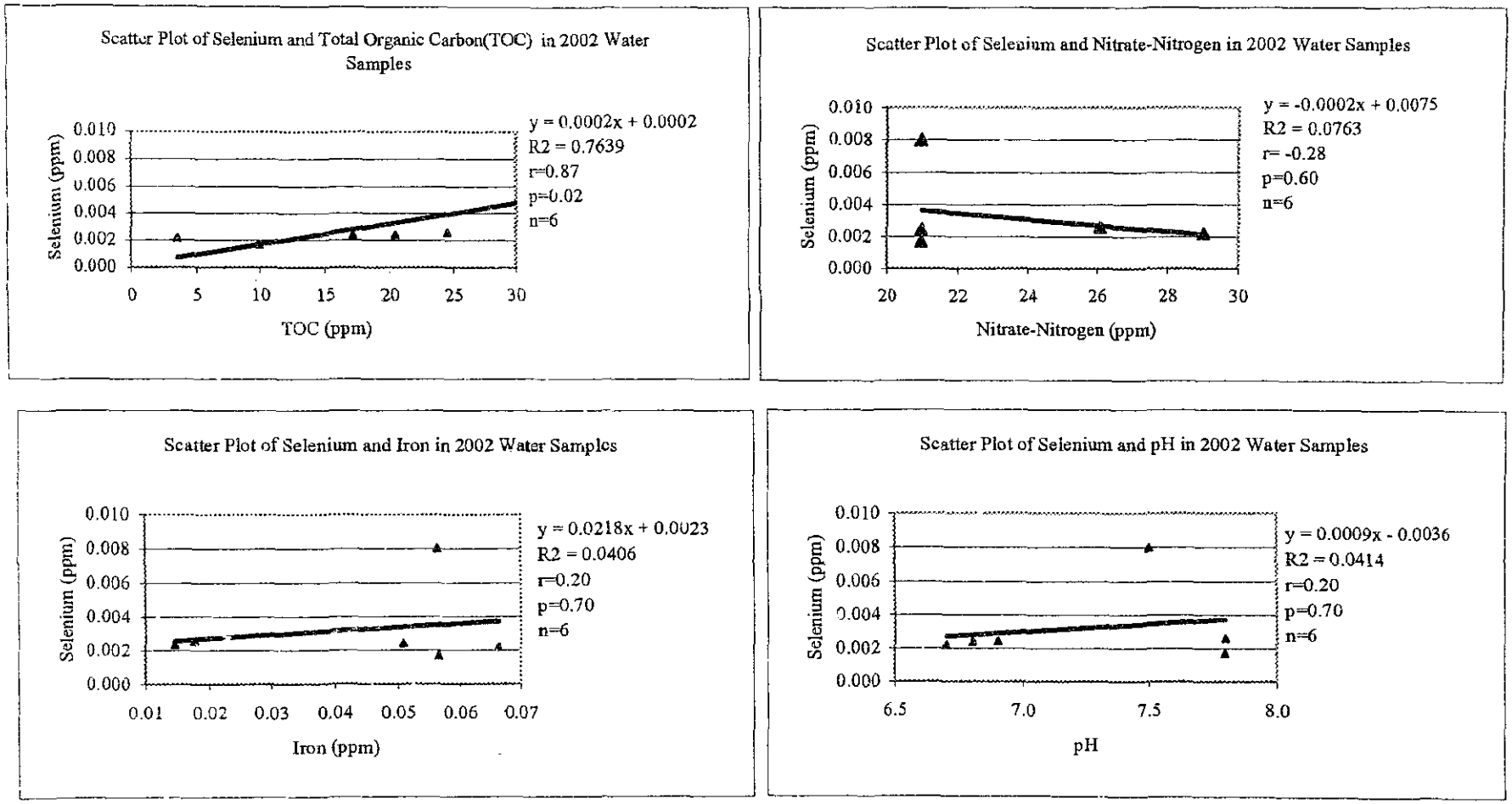


Figure 18. Scatter Plot of Se with TOC, Nitrate-Nitrogen, Iron, and pH in 2002 Water Samples

Soil Sample Analysis
2001 Soil Samples

Sixty three (63) soil samples were collected from the ranch area in August 2001. Most of the samples were from the eastern most part of the ranch. This area is highlighted due to the presence of the selenium indicator plant *Astragalus*. Soil samples were also collected from the soil moisture sampling sites in the westernmost part of the ranch area. Soil solution was extracted from the collected soil samples using two different soil solution extraction methods:

1. Hot water extraction method (Neve, 1980).
2. Digestion with Aqua Regia and Hydrofluoric Acid in a Closed Vessel (Hossner, 1996)

Chemical Analysis of 2001 Soil Samples (Hot Water Extraction)

The collected sixty three soil samples were prepared and run using hot water extraction method (Appendix D). The collected soil extracts were analyzed for different chemical elements (Appendix G). The chemical analysis results were statistically analyzed and summarized in Table 6.

Summary of Chemical Analysis of 2001 Soil Samples (Hot Water Extraction). The concentration of selenium and arsenic are relatively low as the soil extracts were not prepared using acid pretreatment. It is supposed that a significant portion of water soluble selenium (mostly selenate) is not in the selenite form, the only species that can be measured by HGAAS.

Table 6. Statistical parameters for chemical analysis data of 2001 Soil Samples of hot water extraction (n=63)

Parameters	Average	Maximum	Minimum	Std. Dev	Linear Correlation Coefficients (r) with Respect to Selenium	Significance F/ p value
Ca(mg/kg)	708.01	4564.86	64.45	1189.49	0.11	0.40
Mg (mg/kg)	68.77	700.44	2.15	132.95	0.27	0.02
Na (mg/kg)	447.92	7227.57	7.11	1055.04	0.52	0.00001
K (mg/kg)	0.38	21.61	BD	2.74	ND	ND
Fe (mg/kg)	52.95	331.74	BD	75.44	0.30	0.01
Mn (mg/kg)	0.19	1.02	0.01	0.24	0.29	0.02
Cu (mg/kg)	0.16	0.59	BD	0.12	0.40	0.001
Mo (mg/kg)	0.30	2.24	BD	0.37	0.26	0.03
Zn (mg/kg)	0.23	0.91	0.04	0.21	0.30	0.01
P (mg/kg)	1.88	9.49	BD	1.90	0.22	0.08
As(µg/kg)	40.14	136.92	1.97	39.58	0.34	0.006
Se(µg/kg)	10.80	54.91	0.20	12.44	Dependent Variable	

Selenium has significant positive correlations (Figure 19, Figure 20, and Figure 21) with sodium (r=0.52, p=0.00001), magnesium (r=0.27, p=0.02), arsenic (r=0.34, p=0.0.006), manganese (r=0.29, p=0.02), iron (r=0.30, p=0.01, phosphorus (r=0.22, p=0.08), copper (r=0.40, p=0.001), and zinc (r=0.30, p=0.01). Selenium maintains a positive significant correlation with elevation (r=0.25, p=0.05). Selenium has a significant negative correlation with depth (r= -0.23, p=0.06). The scatter plot and

regression analysis of selenium and calcium ($r=0.11$, $p=0.40$) shows that there is very little positive correlation or no correlation between them.

The important points of chemical analysis of soil sample 2001 (hot water extraction) are:

1. High selenium content is significantly positively correlated to high sodium.
2. High selenium is positively correlated to high arsenic content.
3. No distinct depth variation of selenium is found. But, selenium is negatively correlated to depth. In contrast to depth, selenium has a significant positive correlation with elevation.
4. Selenium has significant positive correlation with magnesium, manganese, phosphorus, iron, copper, zinc, and molybdenum.
5. Selenium has insignificant poor positive correlation or no correlation with calcium.

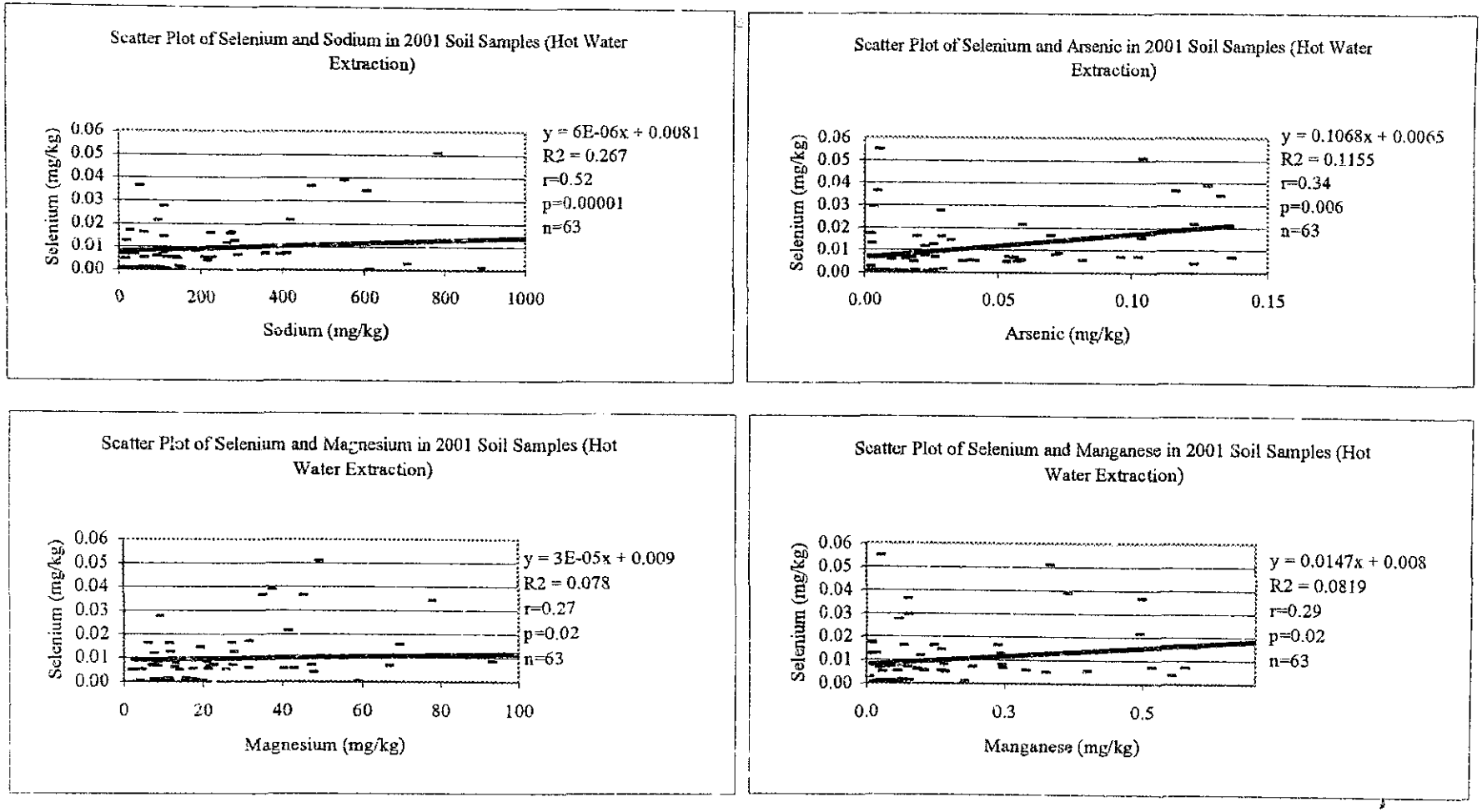


Figure 19. Scatter Plot of Se with Sodium, Arsenic, Magnesium, and Manganese in 2001 Soil Samples (Hot Water Extraction)

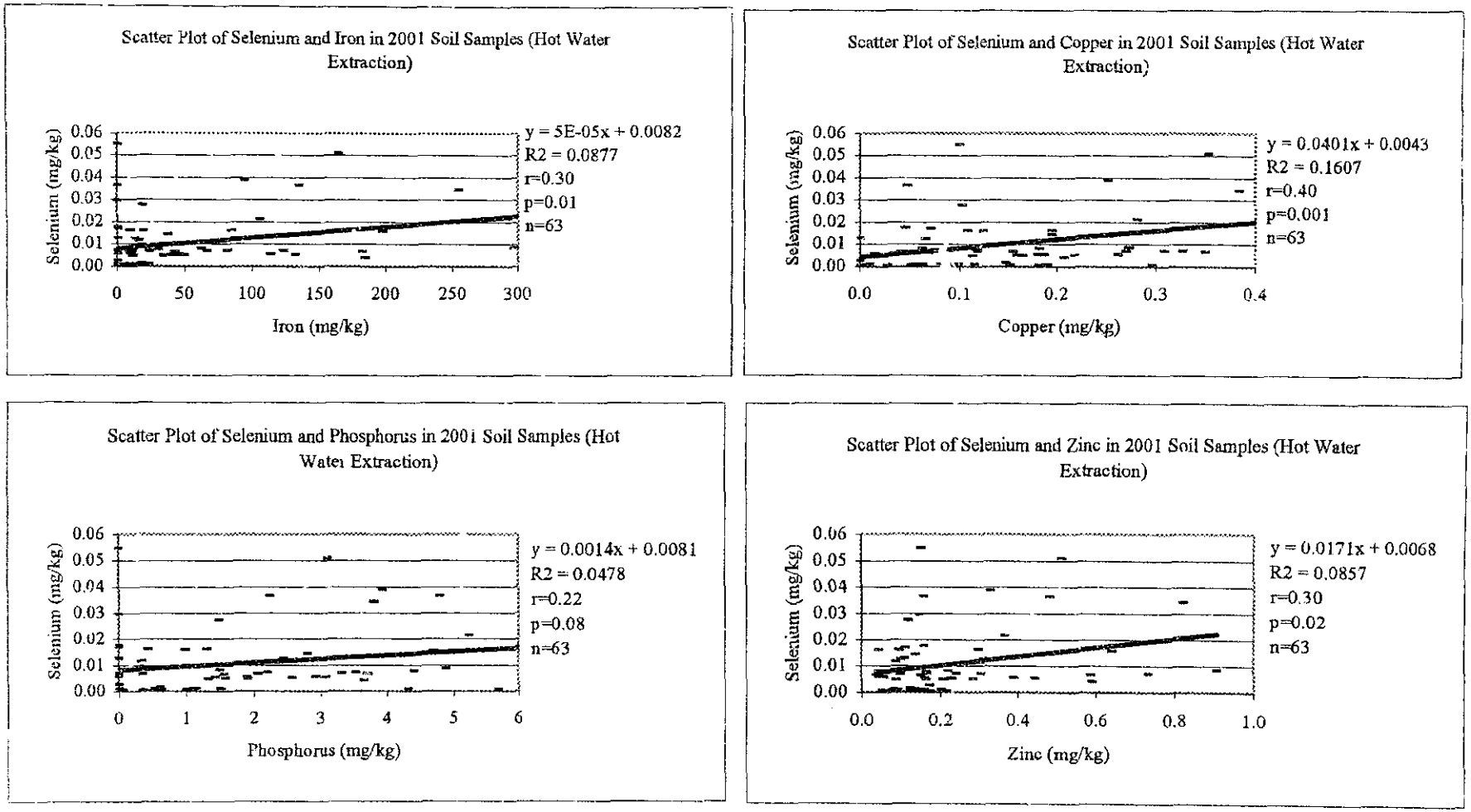


Figure 20. Scatter Plot of Se with Iron, Copper, Phosphorus, and Zinc in 2001 Soil Samples (Hot Water Extraction)

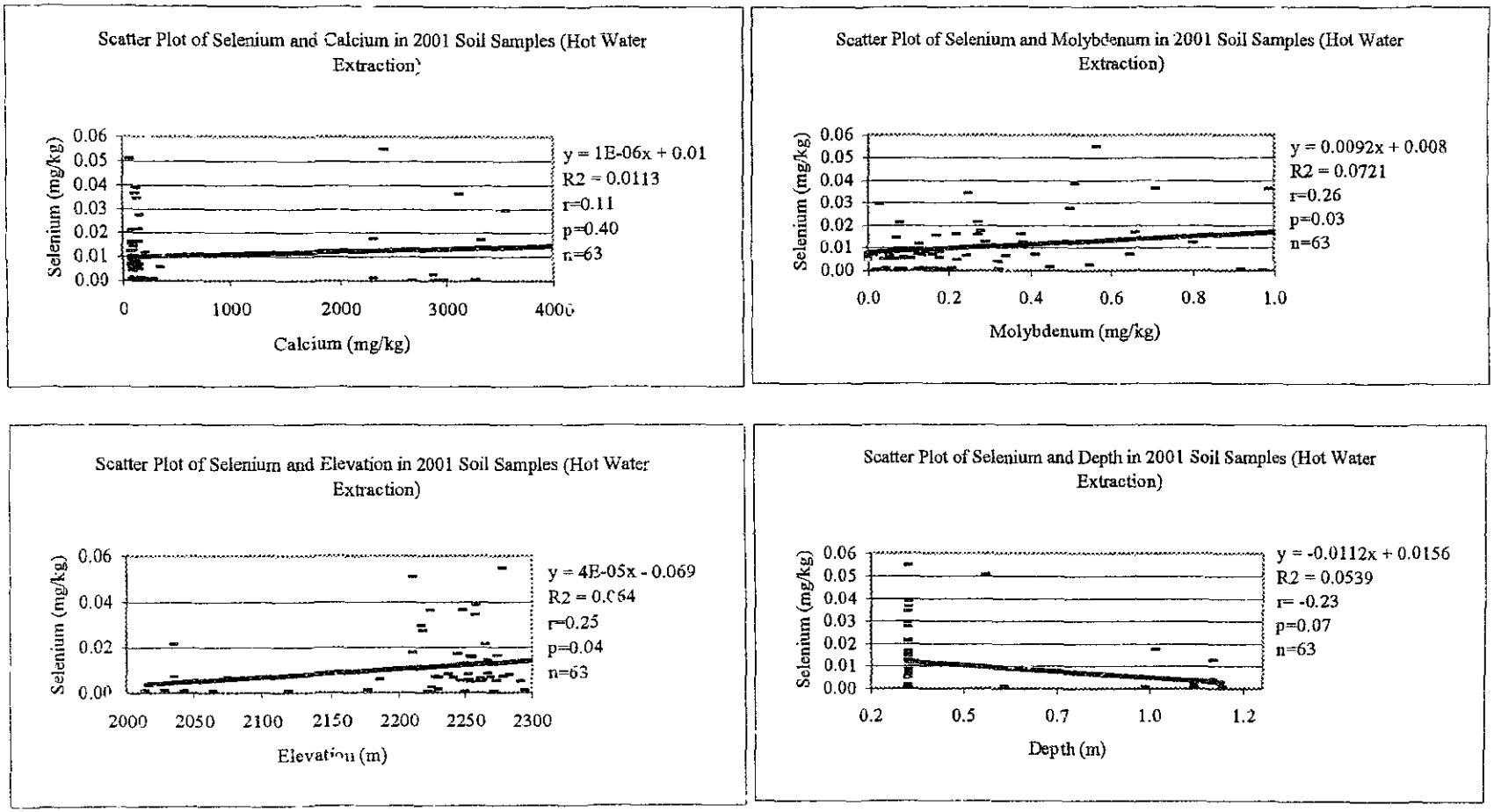


Figure 21. Scatter Plot of Se with Calcium, Molybdenum, Elevation, and Depth in 2001 Soil Samples (Hot Water Extraction)

Chemical Analysis of 2001 Soil Samples (Acid Extraction)

Twenty-two soil samples from 2001 Soil Samples were selected for acid digestion. Soil extracts were prepared for total amount of chemical elements including total selenium and total arsenic in the soil samples (Appendix H). The chemical analysis results were statistically analyzed and summarized in Table 7.

Table 7. Statistical parameters for chemical analysis data of 2001 Soil Samples of acid extraction(n=22).

Parameters	Average	Maximum	Minimum	Std. Dev	Linear Correlation Coefficients (r) with respect to Se	Significance F/ p value
Ca(mg/kg)	67588.2	388818.92	15085.63	75524.41	0.23	0.31
Mg (mg/kg)	25631.60	31245.16	20919.08	2705.04	0.17	0.43
Na (mg/kg)	1350.93	2680.95	554.27	453.63	0.49	0.02
K (mg/kg)	18321.69	22732.86	8619.24	3990.15	0.10	0.64
Fe (mg/kg)	86706.07	99894.56	77532.37	5179.25	0.14	0.55
S (mg/kg)	4235.14	36622.91	508.17	9045.15	0.90	<0.00000002
Mn (mg/kg)	8894.11	31572.5	3368.98	5481.46	0.18	0.43
Cu (mg/kg)	175.75	252.18	10.09	53.09	0.39	0.07
Mo (mg/kg)	6.51	24.80	0.10	6.13	0.38	0.08
Zn (mg/kg)	30.30	40.25	21.08	3.99	0.38	0.08
P (mg/kg)	523.34	700.05	231.44	107.10	0.34	0.12
As(mg/kg)	12.40	19.06	9.4	2.01	0.04	0.87
Se(mg/kg)	1.89	10.24	0.53	2.08		

Summary of Chemical Analysis of 2001 Soil Samples (Acid Extraction). The concentration of total selenium and total arsenic is very high in these soil samples and only a little portion of these are water soluble. The spatial distribution of both total

selenium and total arsenic is similar over the ranch area as it is evidenced from their average concentration and standard deviation in the soil samples.

Total selenium has significant positive correlation (Figure 22, Figure 23, and Figure 24) with total sulfur (r=0.90, p=0.00000002), total sodium (r=0.49, p=0.02), copper (r=0.39, p=0.07), molybdenum (r=0.38, p=0.07), and zinc (r=0.38, 0.08). Total selenium has no correlation (Figure 24) with total arsenic (r=0.04, p=0.87). Total selenium has insignificant positive correlation with potassium (r=0.10, p=0.64), magnesium (r=0.17, p=0.43), manganese (r=0.18, p=0.43), and iron (r=0.14, p=0.55). Total selenium has a relatively significant negative correlation with phosphorus (r= -0.34, p=0.12). The important points of the chemical analysis of the 2001 Soil Samples (acid extraction) are:

1. High selenium content is strongly correlated to sulfur.
2. Total selenium is not correlated with total arsenic content.
3. Total selenium is significantly positively correlated to Zn, Mo, and Cu.
4. Total selenium has a negative correlation with total phosphorus.
5. No distinct spatial variation of total selenium and total arsenic.
6. Only a little portion of total selenium and total arsenic is water soluble (it is evidenced from the data of water soluble portion of selenium and arsenic in the same soil samples of hot water extraction).

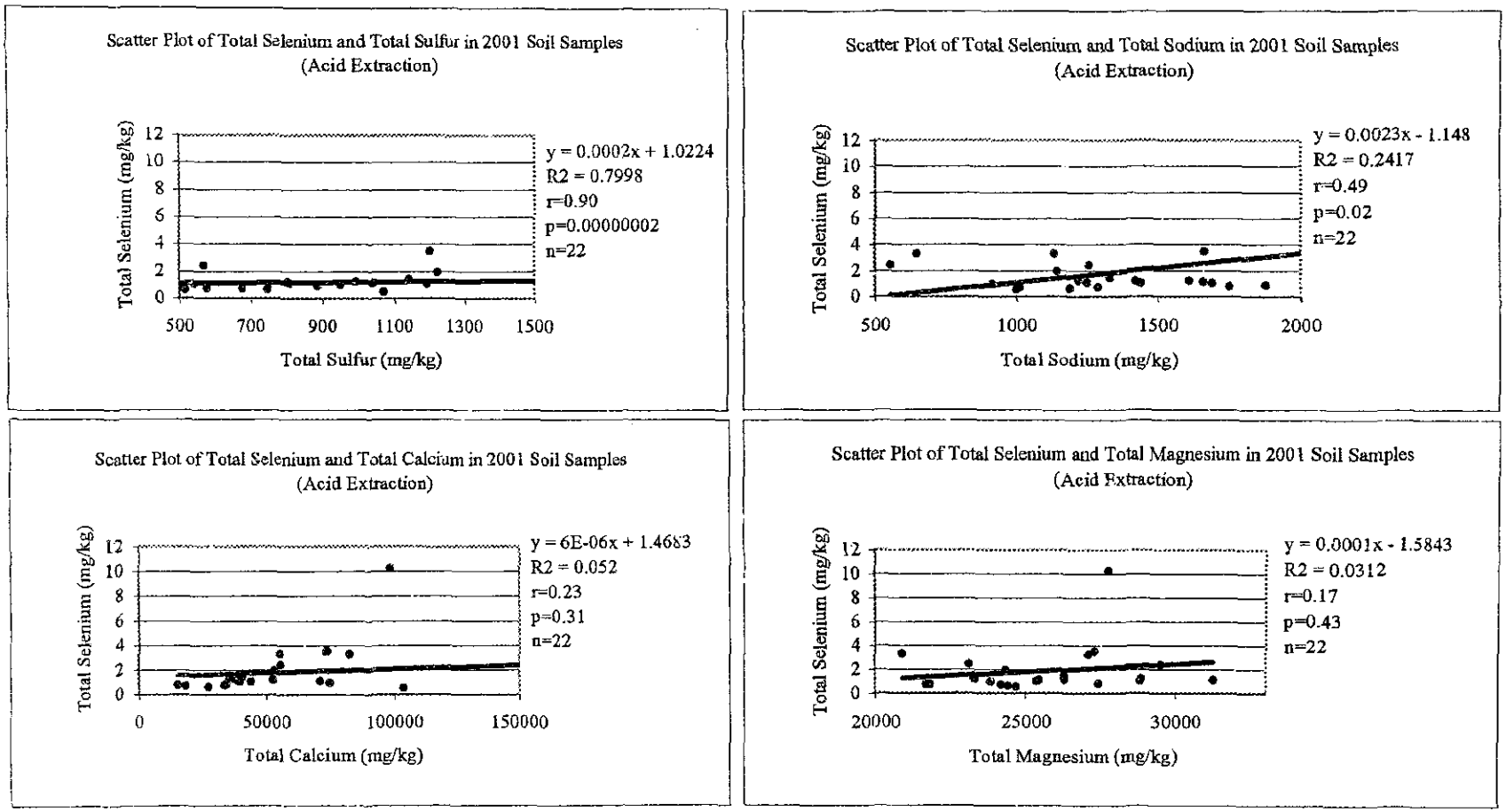


Figure 22. Scatter Plot of Se with Sulfur, Sodium, Calcium, and Magnesium in 2001 Soil Samples (Acid Extraction)

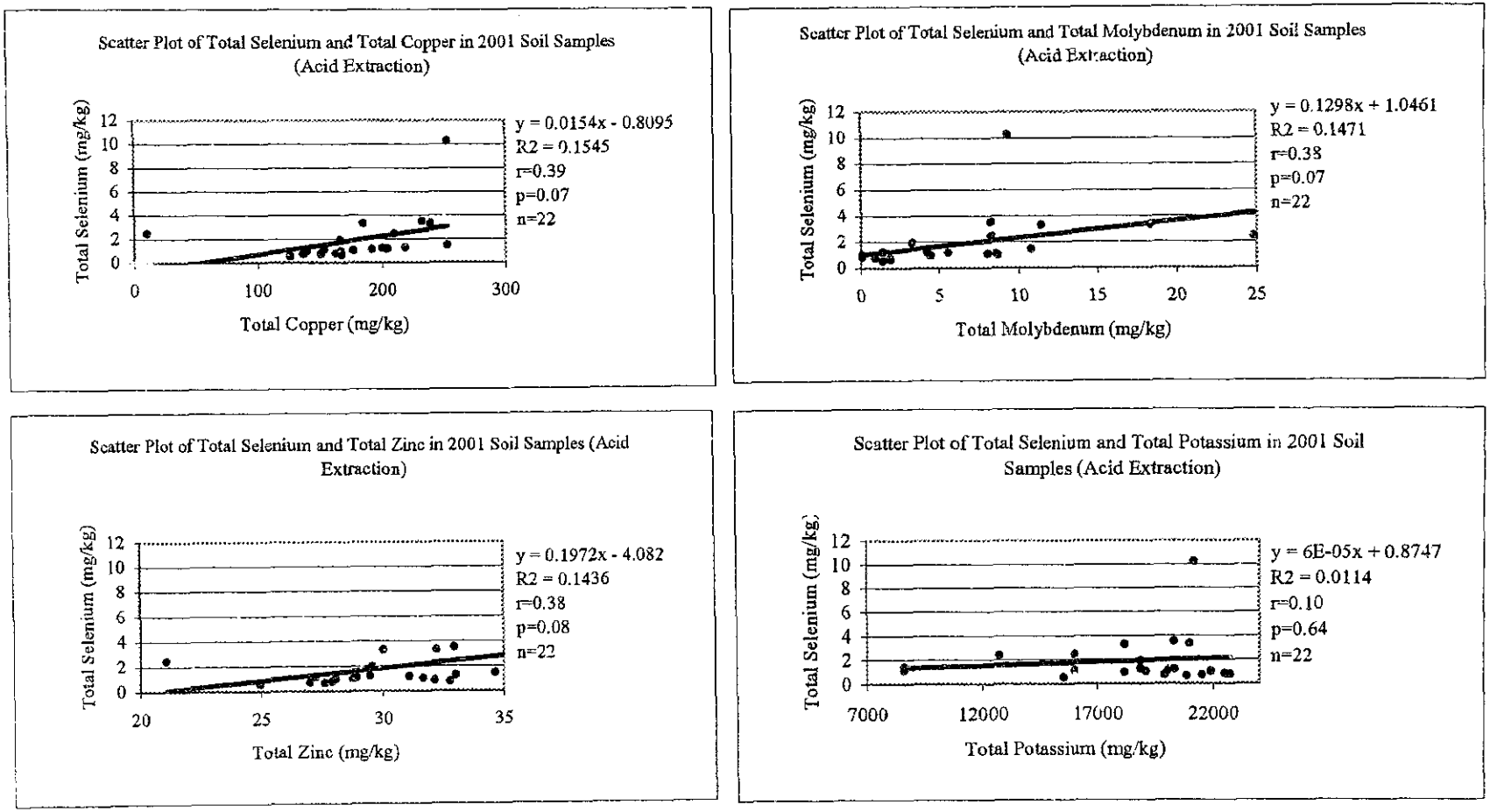


Figure 23. Scatter Plot of Se with Copper, Molybdenum, Zinc, and Potassium in 2001 Soil Samples (Acid Extraction)

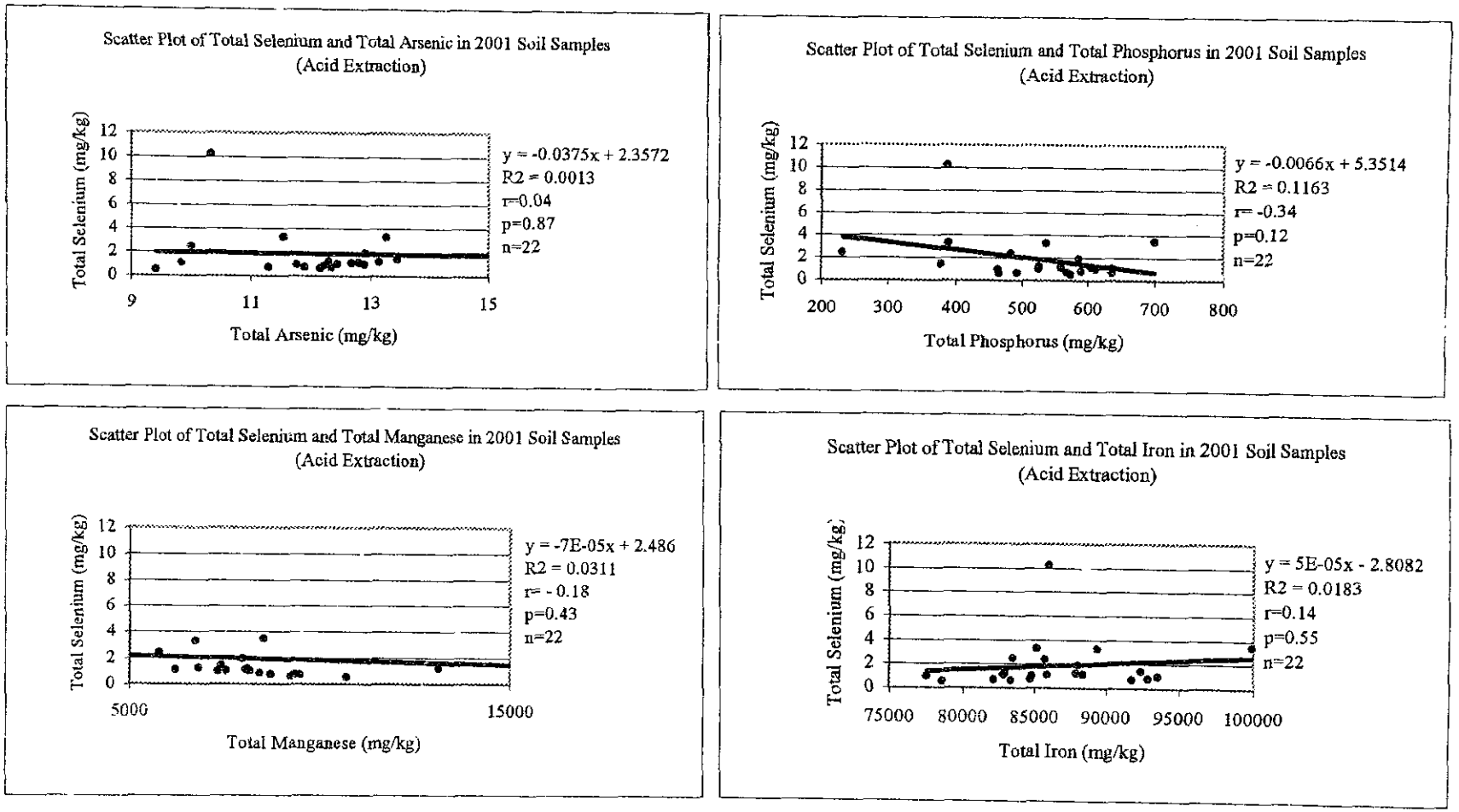


Figure 24. Scatter Plot of Se with Arsenic, Phosphorus, Manganese, and Iron in 2001 Soil Samples (Acid Extraction)

2002 Soil Samples

Thirty-two soil samples were collected in August 2002. These samples include:

1. Two depth profile sampling (0-3.5m and 0-2m).
2. Other locations were sampled twice at a depth of 0.5 m and 1 m respectively.

Soil solution was extracted from the collected soil samples using two different extraction methods:

2. Saturated Paste extraction method (Spackman et al., 1994).
3. Digestion with Aqua Regia and Hydrofluoric Acid in a Closed Vessel (Hossner, 1996).

Chemical Analysis of 2002 Soil Samples (Saturated Paste Extraction)

The thirty-two soil samples were prepared and run using saturated paste extraction method. Saturated Paste Extraction was used to measure the water soluble portion of chemical elements in the soil samples. The collected soil extracts were analyzed for different chemical elements (major anions, cations, TOC, together with selenium, etc.). The complete chemical analysis data set is in Appendix I. Water soluble portion of selenium was measured by using both GFAAS and HGAAS techniques. For HGAAS, soil extracts were further prepared (pre acid treatment) by converting all forms of selenium into the HGAAS measurable form (selenite). GFAAS techniques uses concentrated hydrochloric acid and matrix modifier (nickel nitrate) to ensure total water soluble form of selenium to be converted into GFAAS measurable form (selenite). There was much variation between the results of the two methods. The variation of the selenium concentration of the two methods may be due to the differing rates of oxidizing capacity

and finally reducing them to selenite. The chemical analysis results (Appendix I) were statistically analyzed and summarized in Table 8.

Summary of Chemical Analysis of 2002 Soil Samples (Saturated Paste Extraction). Although there is much variation between the two selenium results from GFAAS and HGAAS, the overall trend of distribution of selenium concentration over the area was more or less similar.

Selenium has significant positive correlation (Figure 25, Figure 26, Figure 27) with sodium ($r=0.47$, $p=0.008$), sulfate ($r=0.3$, $p=0.1$), and sulfur ($r=0.43$, $p=0.01$). Selenium has insignificant positive correlation with nitrate-nitrogen ($r=0.32$, $p=0.16$) and magnesium ($r=0.12$, $p=0.54$). Theoretically organic matter is one of the major sinks for selenium in many parts of the world (MacGregor, 1997). Organic matter as organic carbon ($r=0.38$, $p=0.13$) for this research shows relatively significant positive correlation with selenium. Selenium has significant negative correlation with phosphorus ($r= -0.37$, $p=0.04$) in most of the samples (Figure 25). Selenium has no significant correlation (Figure 25) with depth ($r=0.13$, $p=0.46$). Selenium has insignificant poor negative correlation or no correlation (Figure 26) with calcium ($r= -0.11$, $p=0.56$).

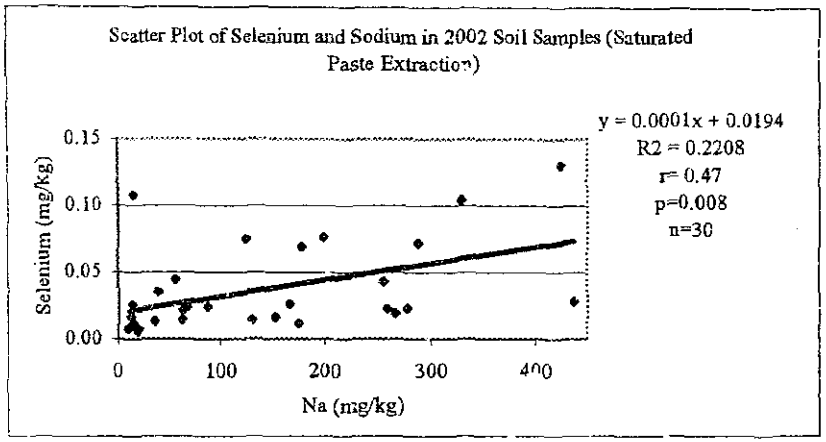
Attempts were taken to determine the selenite and selenate species in the soil samples. No HCl was added to the soil extracts and run for HGAAS. The selenium concentration was below detection limit and ensures no or very little selenium is present as selenite in the saturated paste extracts.

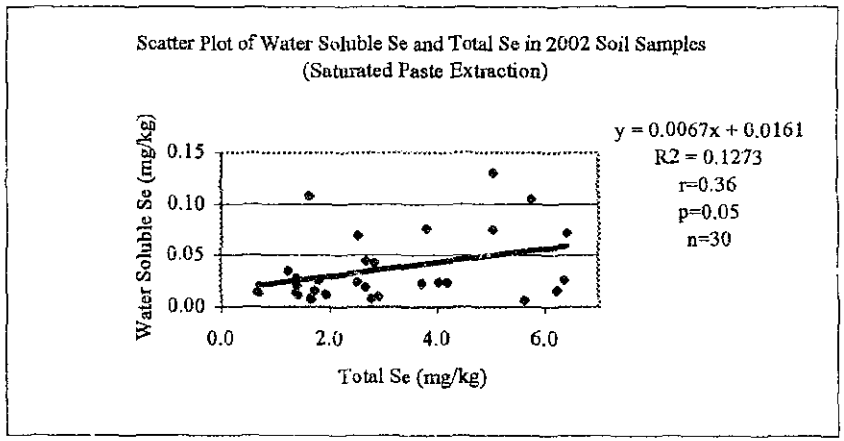
Table 8. Statistical parameters for chemical analysis data of 2002 Soil Samples of saturated paste extraction(n=32).

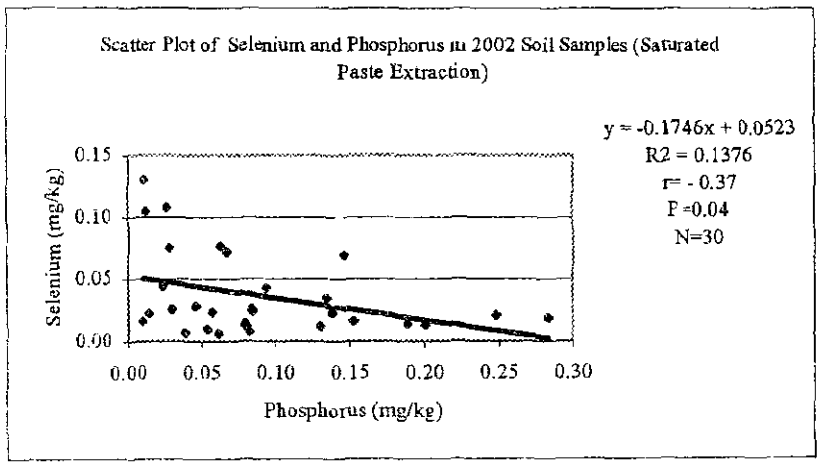
Parameters	Average	Maximum	Minimum	Std. Dev	Linear Correlation Coefficients (r) with Respect to Selenium	Significance F/ p value
Cl (mg/l)	94.17	1594.4	8.3	277.75	0.07	0.14
NO_3-N (mg/l)	0.46	2.47	BD	0.64	0.32	0.16
SO_4^{2-}(mg/l)	4714.46	8458.89	114.8	2540.63	0.30	0.1
PO_4^{3-}(mg/kg)	0.13	0.25	BD	0.08	ND	ND
IC(mg/l)	8.54	15.63	3.20	3.27	ND	ND
P (mg/l)	0.09	0.28	BD	0.07	-0.37	0.04
S (mg/kg)	1331.25	3748.07	32.19	841.91	0.43	0.01
Ca(mg/l)	1059.02	1807.38	135.38	436.59	-0.11	0.56
Mg (mg/l)	302.58	777.84	8.04	273.99	0.12	0.54
Na (mg/l)	154.54	436.23	10.55	136.31	0.47	0.008
K (mg/l)	19.21	61.88	BD	19.52	0.04	0.81
Fe (mg/l)	0.05	0.17	BD	0.04	-0.04	0.08
Mn (mg/l)	9.88	129.66	0.09	24.12	0.12	0.52
Cu (mg/l)	0.18	0.52	0.01	0.13	-0.19	0.32
TOC	1.18	2.13	0.54	0.52	0.38	0.13
Mo (mg/l)	0.19	0.84	BD	0.20	0.20	0.29
Zn (mg/l)	0.01	0.04	BD	0.01	0.23	0.21
Se(ppb)_GF	84.15	698.77	1.3	168.14	ND	ND
Se(ppb)_HG	61.65	455.66	6.15	103.39		
Total Se(ppm) [from acid digested soil sample, 2002]	3294.59	7491.94	704.10	1940.42	0.36	0.05
Se (%) water soluble	1.74	8.11	0.11	1.83	ND	ND

The most important points of the chemical analysis of 2002 Soil Samples (saturated paste extraction) are:

1. High selenium content is strongly correlated to high sodium, sulfate, and sulfur.
2. Selenium has positive correlation with organic matter.
3. No correlation between selenium and depth.
4. Selenium has significant negative correlation with phosphorus.
5. Very little or no selenium is present as selenite.
6. Selenium has insignificant positive correlation with nitrate-nitrogen.
7. Selenium has no correlation with calcium.







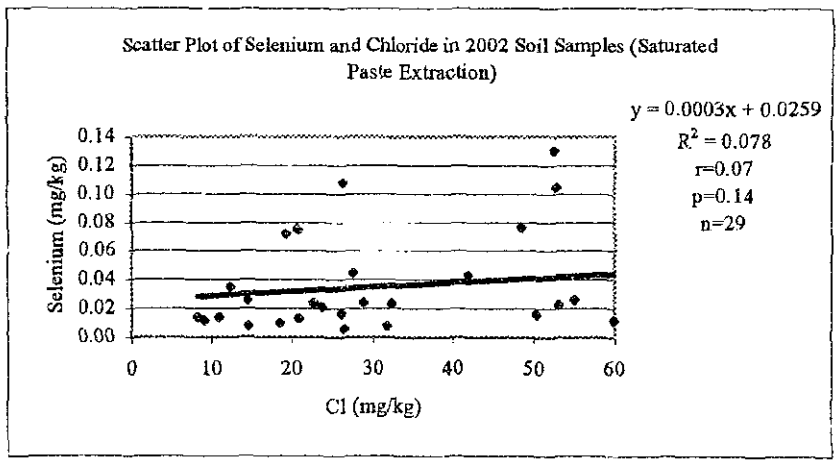


Figure 25. Scatter Plot of Se with Sodium, Total Se, Phosphorus, and Chloride in 2002 Soil Samples (Saturated Paste Extraction)

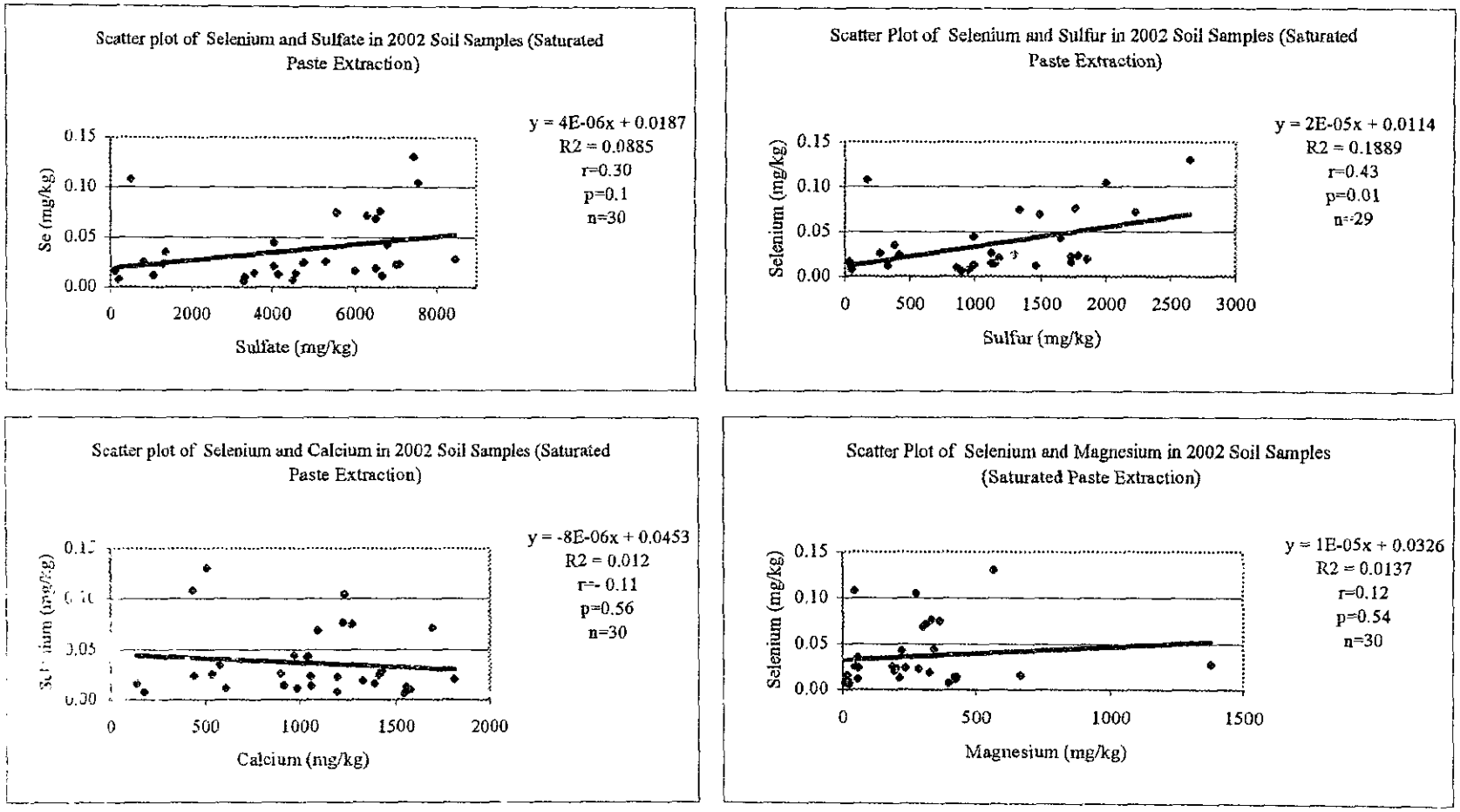


Figure 26. Scatter Plot of Se with Sufate, Sulfur, Calcium, and Magnesium in 2002 Soil Samples (Saturated Paste Extraction)

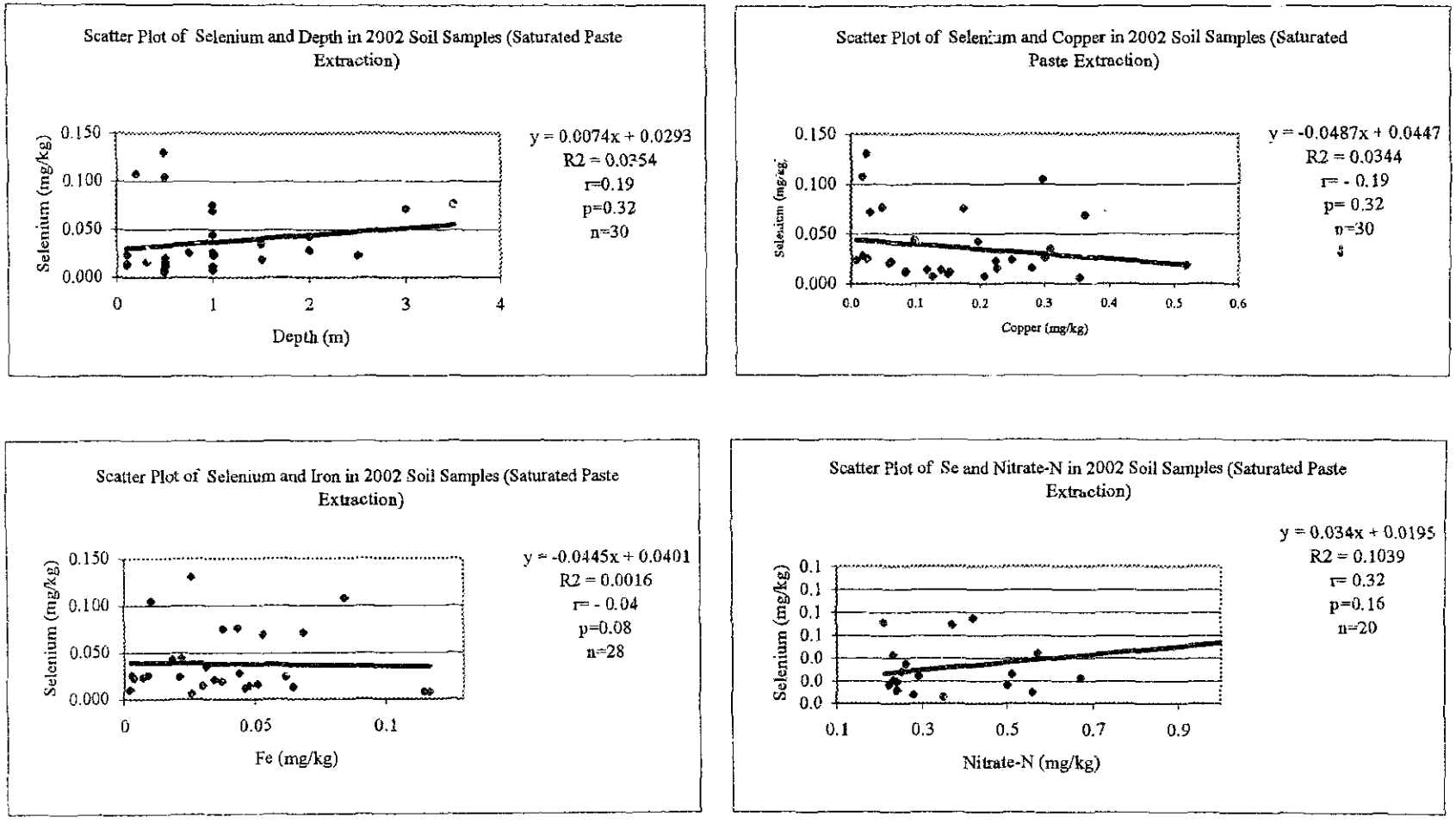


Figure 27. Scatter Plot of Se with Depth, Copper, Iron, and Nitrate-Nitrogen in 2002 Soil Samples (Saturated Paste Extraction)

Chemical Analysis of 2002 Soil Samples (Acid Digestion)

The collected thirty two soil samples were prepared and run using acid digestion method. The acid digestion method ensures the total amount of chemical elements in the soil samples. The collected soil extracts were analyzed for different chemical elements. The complete chemical data set is in Appendix J. The chemical analysis results (Appendix J) were statistically analyzed and summarized in Table 9.

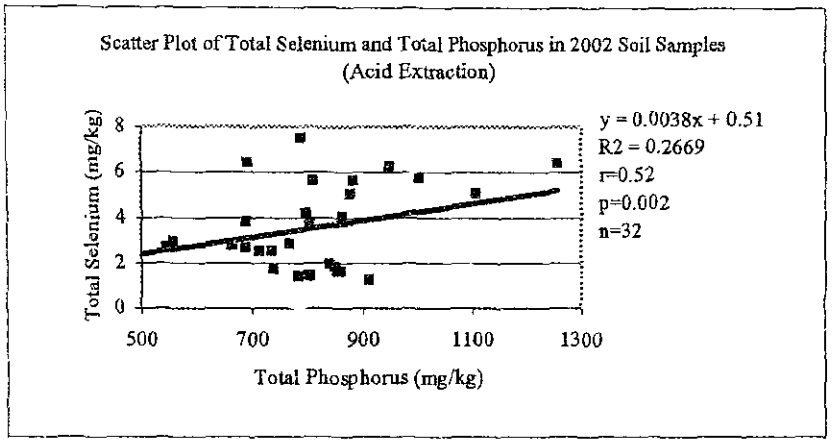
Table 9. Statistical parameters for chemical analysis data of 2002 Soil Samples (acid extraction)

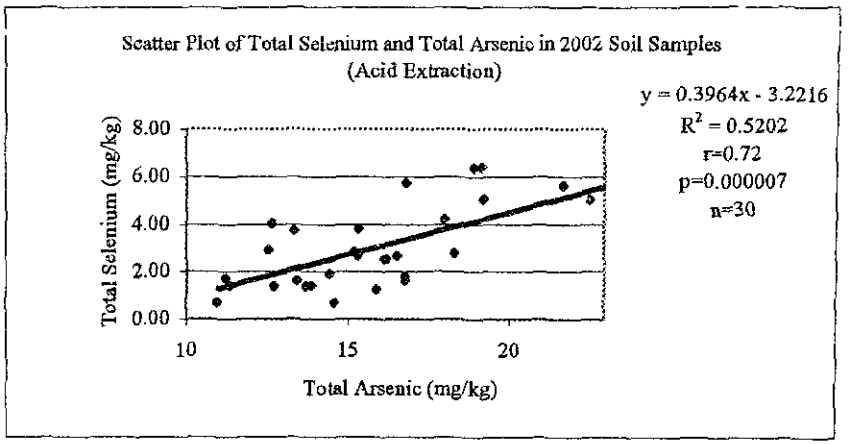
Parameters	Average	Maximum	Minimum	Std. Dev	Linear Correlation Coefficients (r) with Respect to Selenium	Significance F/ p value
Ca(mg/kg)	82938.31	283004.88	27448.18	54019.37	0.44	0.01
Mg (mg/kg)	28150.40	83342.11	13673.45	10801.70	0.33	0.06
Na (mg/kg)	1416.72	2437.97	823.83	439.65	0.21	0.23
K (mg/kg)	19654.08	24549.91	11593.13	2413.15	0.15	0.40
Fe (mg/kg)	99057.50	123516.74	59180.49	13139.10	0.25	0.16
S (mg/kg)	7333.59	56571.64	509.29	10211.88	0.12	0.50
Mn (mg/kg)	8567.04	21469.98	4328.55	4095.11	0.22	0.23
Cu (mg/kg)	236.15	654.78	24.69	111.04	0.30	0.09
Mo (mg/kg)	16.58	70.96	0.57	15.92	0.42	0.01
Zn (mg/kg)	39.89	58.00	29.28	6.80	0.24	0.18
P (mg/kg)	742.03	1256.08	9.89	267.15	0.52	0.002
As(mg/kg)	15.66	27.22	10.25	3.74	0.44	0.01
Se(mg/kg)	3.29	7.49	0.70	1.94		
Depth (m)	0.96	3.5	0.1	0.84	0.09	0.60

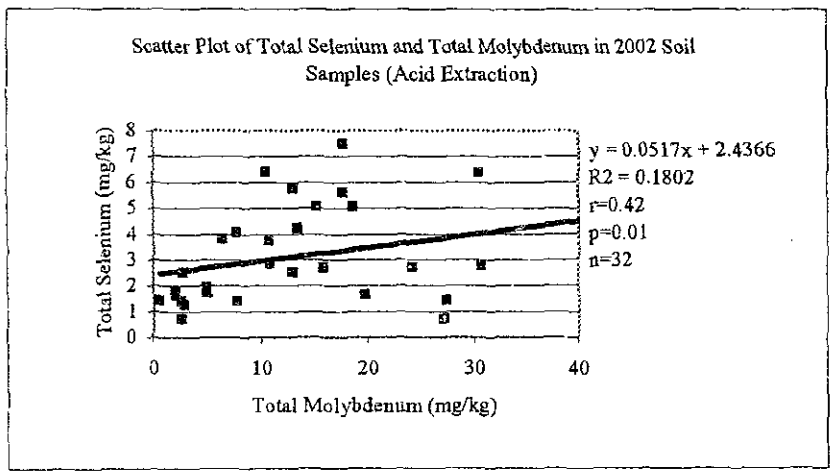
Summary of Chemical Analysis of 2002 Soil Samples (Acid Extraction). No distinct spatial variation of total selenium and total arsenic is found in the area. The range of total concentration of selenium is within a standard deviation of 1.94 ppm. There is no distinct depth variation of total selenium in the area. High selenium content is significantly

positively correlated (Figure 28, Figure 29) to high phosphorus ($r=0.52$, $p=0.002$), calcium ($r=0.44$, $p=0.01$), magnesium ($r=0.33$, $p=0.06$), arsenic ($r=0.72$, $p<0.00001$), iron ($r=0.39$, $p=0.03$, and molybdenum ($r=0.42$, $p=0.09$). Total selenium has no significant correlation (Figure 29) with sodium ($r=0.21$, $p=0.23$), sulfur ($r=0.12$, $p=0.50$). Very little total selenium (1.74% on an average) is water soluble (comparing the water soluble and total selenium in the 2002 Soil Samples). Total selenium has no correlation (Figure 30) with depth ($r=0.09$, $p=0.60$). Water soluble selenium is significantly positively correlated to total selenium ($r=0.51$, $p=0.003$). The important points of the chemical analysis of 2002 Soil Samples (acid extraction) are:

1. Total selenium has insignificant poor positive or no correlation with sulfur and sodium.
2. Total selenium has significant positive correlation with total arsenic, calcium, phosphorus, molybdenum.
3. No correlation between total selenium and depth.
4. Total selenium has poor positive correlation with sodium compared to calcium and magnesium.
5. Only a very small percentage of total selenium is water soluble.
6. No much spatial variation of total selenium and total arsenic over the area. But, for water soluble selenium, the spatial variation is very distinct.
7. High water soluble selenium is significantly positively correlated to high total selenium.







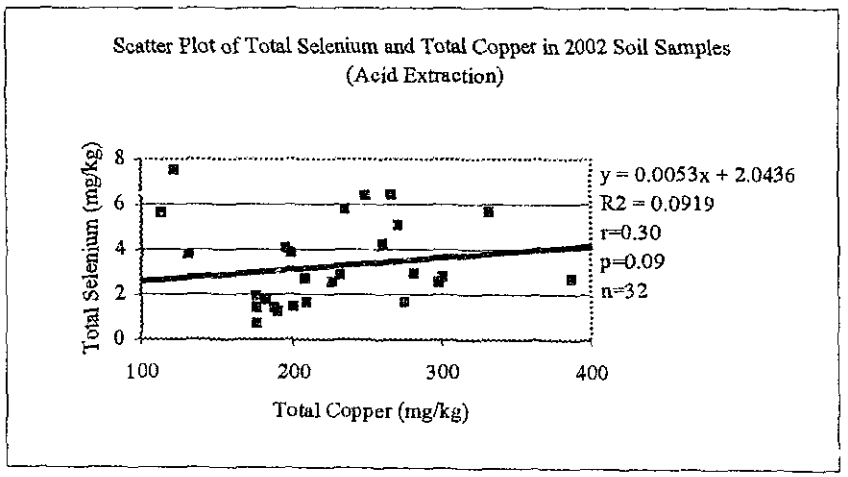
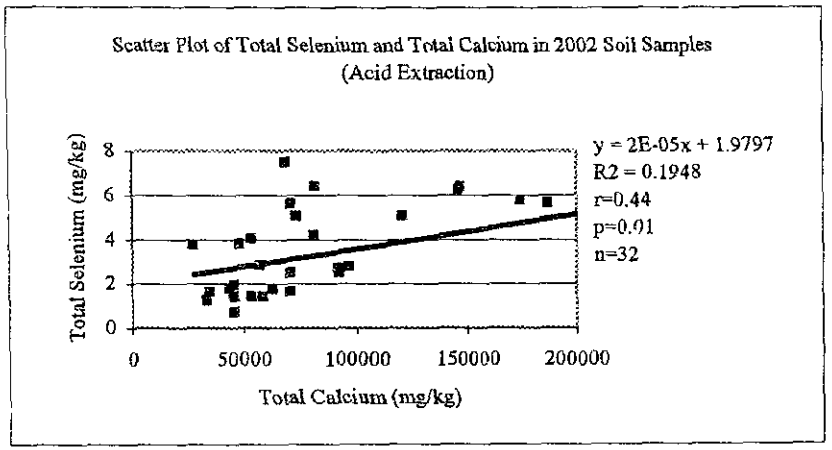
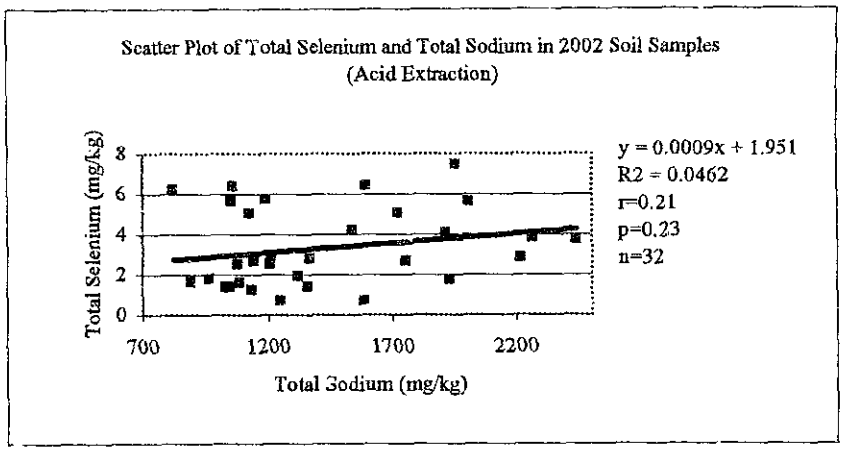
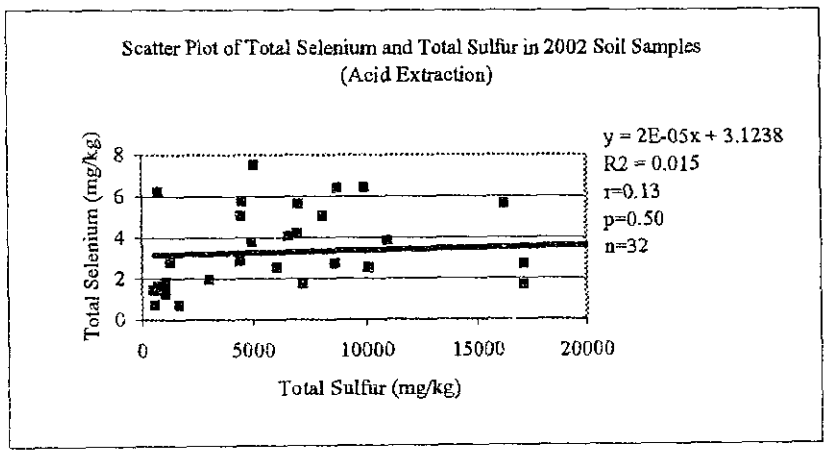


Figure 28. Scatter Plot of Se with Phosphorus, Arsenic, Molybdenum, and Copper in 2002 Soil Samples (Acid Extraction)







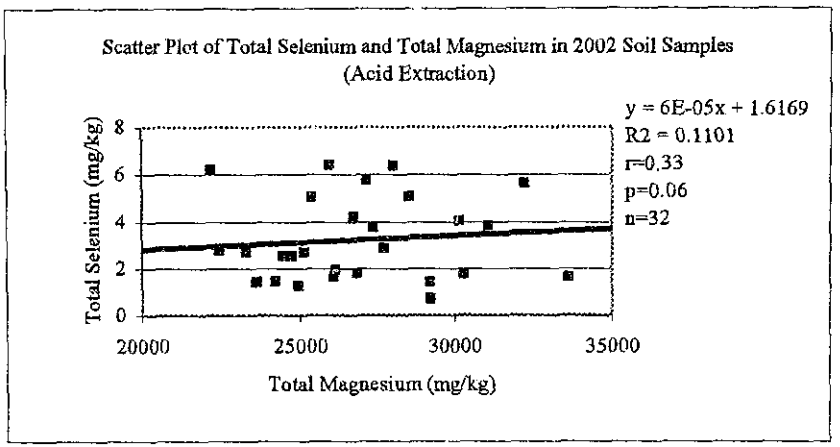


Figure 29. Scatter Plot of Se with Calcium, Sodium, Sulfur, and Magnesium in 2002 Soil Samples (Acid Extraction)

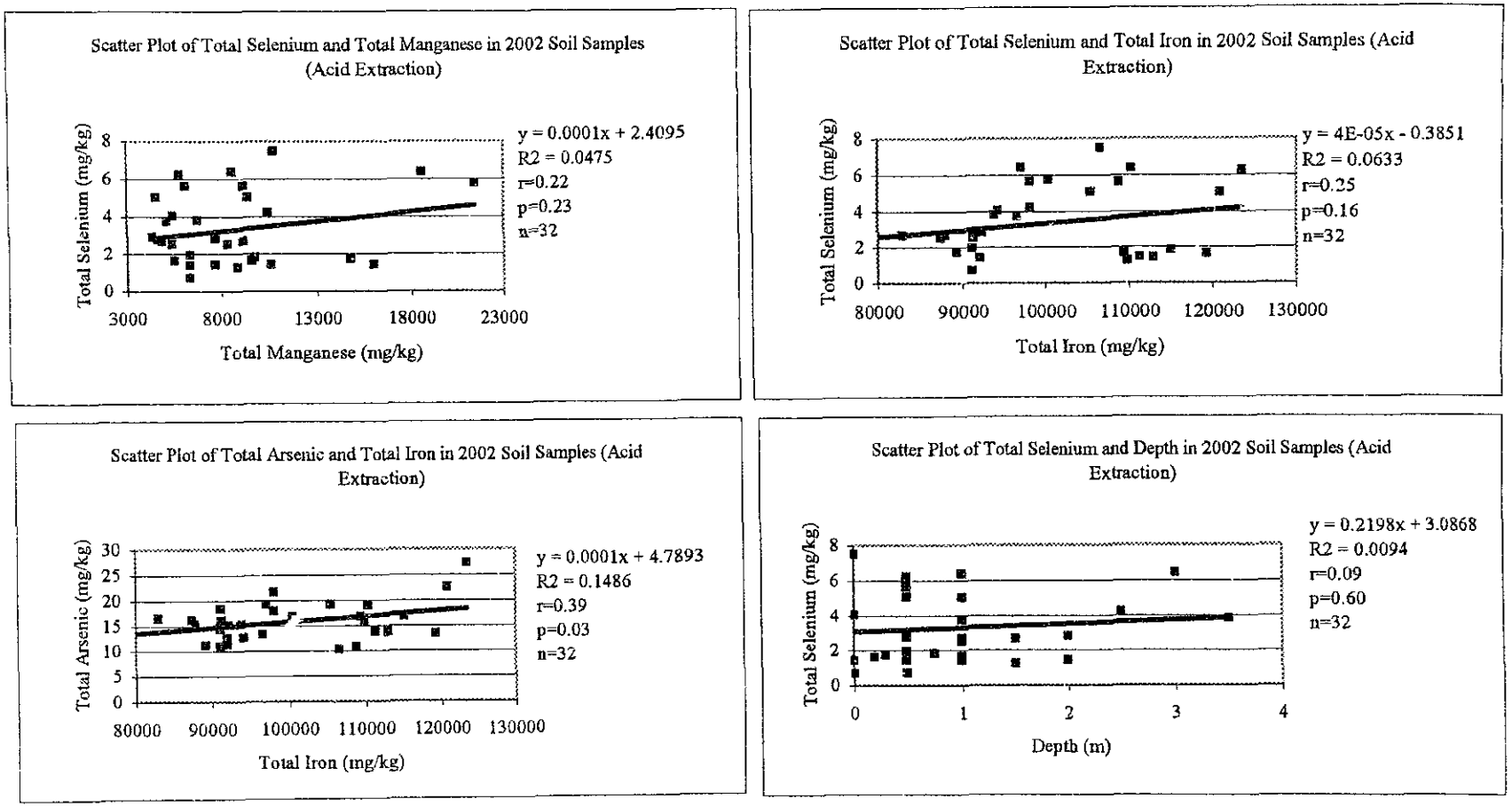


Figure 30. Scatter Plot of Se with Manganese, Iron, and Depth; plot of Arsenic and Iron in 2002 Soil Samples (Acid Extraction)

5.2 HYPOTHESIS TESTING

The results of chemical analyses indicate differing degrees of correlation between selenium and other chemical constituents in the soil and water samples in the research area. This section compares these relationships to hypotheses related to selenium geochemistry that have appeared in the literature. Some of the hypotheses are well supported by the analytical data of this research. On the contrary, some of the hypotheses are not supported, very poorly supported, or opposed by the results. A short discussion of these hypotheses related to selenium and other chemical elements in the research area follow.

Hypothesis 1: High selenium is generally associated with high dissolved solid concentration (Crist, 1974). This hypothesis is supported by the chemical analysis results of the 2001 Soil Moisture Samples ($r=0.88$, $p=0.0001$), where selenium is significantly positively correlated to high total dissolved solids (as electrical conductance). Selenium is insignificantly positively correlated to 2002 Water Samples ($r=0.53$, $p=0.27$). Soil samples have no electrical conductance data.

Hypothesis 2: Selenium concentration usually increases with depth (Jacobs, 1989). For total selenium no correlation with depth (0 m-3.5 m) is found, but the 2001 Soil Samples ($r=-0.23$, $p=0.06$) show a negative significant correlation between water soluble selenium and depth. A positive significant correlation is found between water soluble selenium and elevation (above mean sea level) of the sampling locations for 2001 Soil Samples ($r=0.25$, $p=0.05$).

Hypothesis 3: Selenium (soluble) concentration will decrease with increasing organic matter (Jacobs, 1989). This hypothesis is rejected by the 2001 Soil Moisture Samples

(r=0.94, p=0.000007 for Soil Moisture August 01, r=0.53, p=0.09 for Soil Moisture August 09, and r=0.83, p=0.04 for Soil Moisture August 27) and 2002 Soil Samples (r=0.38, p=0.13), where selenium shows positive correlation to total organic carbon. For 2002 Water Samples (r=0.25, p=0.63), selenium has insignificant positive correlation with total organic carbon. This may be due to the fact that selenium trapped in the organic matter is mostly water soluble. 2001 Soil Samples were not analyzed for total organic carbon.

Hypothesis 4: Selenium will increase with increasing phosphate (Jacobs, 1989). The concentration of phosphate in 2002 Soil Samples (saturated paste extraction) and 2002 Water Samples were mostly below detection limit.

Phosphorus (P) concentration in 2001 Soil Samples for hot water extraction (r=0.22, p=0.08) and acid extraction (r=0.34, p=0.12), and 2002 Soil Samples for acid extraction (r= 0.52, p=0.002) shows significant positive correlation with selenium. 2002 Soil Samples for saturated paste extraction (r= - 0.37, p=0.04) shows significant negative correlation with selenium.

Hypothesis 5: Selenium commonly occurs in groundwater if only nitrate is present (Weres et al, 1989). All groundwater, surface water, and soil moisture samples have both nitrate-nitrogen and selenium in a measurable quantity. There is significant negative correlation between selenium and nitrate-nitrogen in 2001 Soil Moisture Samples (r=-0.70, p=0.03 for Soil Moisture August 01 and r=-0.60, p=0.1 for Soil Moisture August 09. For 2002 Water Samples, the correlation between selenium and nitrate-nitrogen (r=-0.28, p=0.60) is negative, but insignificant. Whereas, insignificant positive correlation between selenium and nitrate-nitrogen is found in 2002 Soil Samples (r=0.32, p=0.16).

This opposite correlation shows that in soil environment the correlation between selenium and nitrate-nitrogen is positive. But in water environment the correlation between selenium and nitrate-nitrogen is negative.

Hypothesis 6: High selenium is related to high sodium, magnesium, and sulfate (Presser et al., 1990; Frankenberger et al., 1994). This hypothesis is supported by all the samples tested [2002 Water Samples{(r=0.72, p=0.1 for sodium), (r=0.92, p=0.009 for magnesium), and (r=0.58, p=0.23 for sulfate)}, 2001 Soil Moisture Samples {(r=0.86, p=0.0004 for sulfate for Soil Moisture August 01)}, 2001 Soil Samples of hot water extraction{(r=0.52, p=0.00001 for sodium), (r=0.27, p=0.02 for magnesium)}, 2001 Soil Samples of acid digestion {(r=0.49, p=0.02 for sodium), (r=0.17, p=0.43 for magnesium), (r=0.90, p=<0.00000002 for sulfur} and 2002 Soil Samples of saturated paste{(r=0.47, p=0.008 for sodium), (r=0.12, p=0.54 for magnesium), (r=0.30, p=0.1 for sulfate)}, and 2002 Soil Samples of acid digestion{(r=0.21, p=0.23 for sodium), (r=0.33, p=0.06 for magnesium)}]. These samples results show that selenium is positively correlated to sodium and sulfate or sulfur in most of the samples (2001 Soil Moisture, 2002 Water Sample, 2001 Soil Samples, and 2002 Soil Samples. Magnesium has significant positive correlation with selenium in 2002 Water Samples. Whereas, magnesium has insignificant correlation to selenium in soil samples (2001 Soil Samples and 2002 Soil Samples). All these analyses strongly support the possibility that selenium is chemically related to the sulfate salts of mostly sodium in soil samples and salts of sodium and magnesium in water samples.

Hypothesis 7: Gypsum does not seem to tolerate the substitution of selenate for sulfate places (Presser et al., 1990). This hypothesis is strongly supported by the evidence of

the very little or no correlation (insignificant) between selenium and calcium in 2002 Water Samples ($r=0.02$, $p=0.98$), 2001 Soil Samples of hot water extraction ($r=0.11$, $p=0.40$), and 2002 Soil Samples of saturated paste extraction($r= -0.11$, $p=0.56$). But, 2002 Soil Samples of acid extraction ($r=0.44$, $p=0.01$) shows significant positive correlation between selenium and calcium. 2001 Soil Samples of acid extraction show insignificant positive correlation between selenium and calcium ($r=0.23$, $p=0.31$) than Soil sample 2002 of acid extraction.

This contrary result between water soluble and acid digested extracts of soil samples (both 2001 Soil samples and 2002 Soil Samples) suggests that gypsum may have very little or no significance as a sink of water soluble portion of selenium. But gypsum may have important role as a sink for total selenium.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The chemical analyses results suggest that there are differing degrees of correlation between selenium and other chemical constituents. The analytical results statistically support some of the established hypotheses related to selenium with other chemical constituents, but not others. The nature of overall selenium geochemistry together with major anions, cations, organic carbon, etc., is generally similar in both the soil and water system in the area. The water soluble selenium in the soil extracts, water, and soil moisture samples is highly sensitive to the degree of acid treatment (conversion of oxidation state of selenium from selenate to selenite) before analysis by HGAAS. The most important findings of the research include:

1. Both total and water soluble selenium in the soil environment maintains a positive correlation with sodium, sulfate, and sulfur.
2. For total selenium, there is no correlation with depth (0 m-3.5 m), but 2001 Soil Samples show a negative significant correlation between water soluble selenium and depth. A poor positive significant correlation is found between water soluble selenium and elevation for 2001 Soil Samples.
3. Water soluble selenium is mostly selenate. Selenite was below detection limit in the water soluble extracts of soils.
4. Very little amount of total selenium is water soluble, with an average of 2 %.

5. High selenium is related to high arsenic concentration in both the water soluble and acid extracted soil solution. This trend is also true for soil moisture samples.
6. There is little spatial variation of total selenium over the area, but distinct for water soluble selenium.
7. Phosphorus has positive correlation with selenium in the soil samples of hot water and acid extraction. Selenium has significant negative correlation to phosphorus in soil samples of saturated paste extraction.
8. Selenium in the water samples and soil moisture samples are positively correlated to total dissolved solids (measured as electrical conductance).
9. Total organic carbon has positive correlation with selenium concentration.
10. Nitrate-Nitrogen has significant negative correlation with selenium for water and soil moisture samples, but has a positive correlation with selenium for 2002 Soil Samples.
11. Calcium has very little or no correlation with water soluble selenium.
12. All the analytical data suggests that sodium, magnesium and sulfate salts serve as a geochemical sink for water soluble selenium. The solubility of these salts may be the principal factor controlling the mobility and transport of selenium in the soil-water environment.

6.2 Recommendations

To understand the distribution and mobilization of selenium in the water-soil-sediment environments, it is essential to investigate the thorough speciation of selenium with their corresponding phases (i.e. mineral oxide, organic, carbonate, etc.) in the environments. A proper range of sequential extraction techniques for selenium (for soluble fraction, adsorbed fraction, carbonate fraction, organic fraction, total, etc.) can provide valuable information in this respect.

1. It is evident that certain sodium-magnesium-sulfate minerals are the major geochemical sink for selenium. The potential solubility of these minerals plays a major role in selenium mobilization in the environments. The mineralogical composition of the soils and sediments and their X-ray diffraction, X-ray adsorption fine structure (XAFS) spectroscopy and scanning electron microscopy (SEM) can provide an interesting understanding in this point of view.
2. Organic matter in the soil and water has been shown to be another sink for selenium (MacGregor, 1997). It is important to know the form (i.e. fulvic acids, humic acids, etc.) in which selenium is associated with. This will put light to understand the bioavailability and the mobility of the organic selenium.
3. Microbial activity in the soils and waters should be investigated to understand if microbes help mobilize selenium.
4. To understand the geologic source of selenium, boreholes should be drilled at regular intervals in the area and samples should run for total chemical and mineralogical analysis.

5. Stable isotope analysis of selenium in the soil-water-sediment samples can add additional information on the source and sink of selenium in the environments.

APPENDICES

Appendix A. Physicochemical properties of selenium (Frankenberger et al., 1994)

Atomic mass	78.96
Atomic number	34
Electronic configuration	(Ar) 3d104s24p4
Covalent radius	1.16
Atomic radius	1.40
Ionic radius	1.98 A^{O}
Atomic volume, w/d	Amorphous: 18.55; Monoclinic: 17.72; Hexagonal: 16.31-16.50
Density, g/cm3	4.79
Melting point, °C	217
Boiling point, °C	685.4
Hardness, relative units	2
Common oxidative states	-2, 0, +4, +6
Bond energy (M-M), kcal/mole	44
Bond energy(M-H), kcal/mole	67
Ionization potential, eV	9.75
Electron affinity, eV	-4.21
Electronegativity	2.4
Polarizability, cm3x 10-25	105
Latent heat of fusion, J/g (cal/g)	6.91
Heat of vaporization, J/g	272.98
Thermal conductivity, W/(m. °C)	0.293-0.766
Crustal abundance, ppm	0.05-0.14
Abundance in soil, ppm	0.01-100
Maximum permissible limit, ppm	0.01
Radioactive Isotopes	^{70}Se, ^{71}Se, ^{72}Se, ^{73}Se, ^{75}Se(Half life=120.4 days) and ^{79}Se(Half life=65000 yrs), ^{81} Se, ^{83}Se, ^{84}Se
Stable Isotopes	^{74} Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, and ^{82}Se
Dietary Requirements	0.05-0.3 mg/kg of Se
Toxic Vegetation	≥5mg/kg of Se

Appendix B. Selenium concentrations in different rocks and soils

Rock/Soil	Se (mg/kg)	References
Crustal Rock	0.05	Taylor, 1964
Granite	0.01-0.05	Kubata-Pendias and Pendias, 1984a
Sedimentary rocks	0.03-300	Kubata-Pendias and Pendias, 1984a; NAS-NRC, 1983
Shales	0.6	Kubata-Pendias and Pendias, 1984a
Sandstones	0.05-0.08	Kubata-Pendias and Pendias, 1984a
Phosphate rocks	1-300	NAS-NRC, 1976
Limestones and Dolomites	0.03-0.1	Kubata-Pendias and Pendias, 1984a
Cretaceous Black Shales	Upto 300	NAS-NRC, 1983
Coal	0.46-10.7	Pillay et al., 1969
Coal, China	Upto 90000	Yang et al., 1982
Oil	0.06-1.4	Berrow and Ure, 1989
Soils, seleniferous	1-80	Trelease, 1945
Soils, USA	<0.1-4.3	Shacklette & Boerngen, 1984; Tidball, 1984
Soils, England/Wales	<0.01-4.7	Thornton et al., 1983
Soils, Hawaii	6.7-20	Berrow and Ure, 1989
Soils, South Dakota	1.0	Byers, 1935
Cretaceous soils, New Mexico Non-Cretaceous soils, New Mexico	4.6 0.6	Thomas et al., 1998
Maximum Baseline of Se concentration Soils of Northern Great Plains, USA Soils of Western USA	 3.3 1.1	 See et al., 1992
Sun River Area, Montana, USA Western United States	0.1-8.5 0.1-4.3	Nimick et al., 1996
Powder River Basin, USA	0.1-15.2	See et al., 1995
Turtle Lake, New Rockford, Harvey Pumping, Lincoln Valley, LaMoure, North Dakota	<0.1-6.0	Berkas et al., 1996

Appendix C. Selenium concentrations in fresh water systems

Area	Species	Se (µg/L)	Reference
Typical Freshwater	Se(Total)	0.05-5.0	Brett, 1999
	Se(IV)	$1.6X10^{-4}$-0.23	
	Se(VI)	<0.005-0.10	
	Se(II + 0)	0.035-0.48	
Kesterson Reservoir, CA, USA	Se(Total)	65.5-398	Cooke, 1985
	Se(IV)	16-36	
	Se(VI)	7.7-344	
	Se(II + 0)	3.9-93	
Hyco Reservoir, NC, USA	Se(Total)	6.02±0.18	Cutter, 1986
	Se(IV)	3.99±0.12	
	Se(VI)	1.18±0.22	
	Se(II + 0)	8.52±0.24	
Groundwater	Se(Total)	<0.05-27	Cutter, 1986
Drinking Water	Se(Total)	0.12-0.44	
Rain and Snow	Se(Total)	0.005-0.33	Brett, 1999
	Se(IV)	0.005-0.22	
	Se(VI)	<0.002-0.27	
Powder River Basin, Wyoming, USA	Se (Total)	3-125	See et al., 1995
San Joaquin Valley, CA, USA (groundwaters)	Se (Total)	50-1000	Gilliom , 1989

Appendix D: Soil Extraction Methods

Hot Water Extraction Method (Neve, 1980)

Apparatus and Equipments:

1. Reflux beaker and setup
2. Falcon tube
3. Centrifuge
4. Filter papers

Procedures:

1. Weight out 5g of dried, homogenized soil into reflux beaker.
2. Add 30 ml of distilled-deionized into beaker
3. Reflux for half hour
4. Transfer slurry mixture to 50 ml falcon tube (make sure all water is transferred)
5. Centrifuge mix at highest setting in physiology room centrifuge
6. Transfer supernatant through Whatman filter by gravity to new 50 ml Falcon tube (to get rid of roots and other floating debris).

Purpose:

1. Water soluble portion of metals by ICP/GFAAS
2. Water soluble portion of Selenium and arsenic

Selenium Analysis:

The samples were prepared for Se analysis

1. Add 2 mL of 6M HCl to 10 mL of soil extracts

2. The samples were allowed to stand at room temperature for 24 hours before analysis. For As analysis, to 4.75 mL of the Se preparation, 0.75 mL of 5% KI and Ascorbic acid was added. The samples were allowed to stand at room temperature for 24 hours.
3. For other metals except selenium and arsenic, the extracts are run without treatment.

Saturated Paste Extraction Method (Spackman et al., 1994)

Apparatus and Equipments:

1. 500ml plastic containers with cap
2. Spatula
3. Drying cans with lid
4. Desiccator
5. Oven (temperature controlled)
6. 100ml glass bottles

Procedures:

1. Place 200g soil into a plastic container
2. Add DI water (about ½ inch on the soil top)
3. Close the container and keep it for 24 hours
4. Mix the sample with a spatula. The sample will have a consistency of a milk shake
5. Percentage(%)of water of the saturation paste must be determined

- Record the drying can ID with its empty weight
- Place 20g saturated soil extract to the can

- Record the wet weight of the sample and can
- Place the can on an oven at 105°C /222°F for 24 hours
- Place the can in a desiccator until cool
- Record the dry weight
- $H_2O\%$= (Wet weight-dry weight)/(Wet weight) X 100

6. Filter the extraction (from step 4) using a filter press or Buchner filter funnel.
7. Store it at 4°C /39°F in 250/500ml glass bottles

Purpose:

3. To determine pH, EC, anions (Cl^-, SO_4^{-2}, $N0_3$-N^- by IC)
4. Water soluble portion of metals by ICP/GFAAS
5. Water soluble portion of Selenium

Acid treatment and sample preparation for selenium analysis by HGAAS:

1. Add 3ml extract into a 50ml test tube
2. Add 12ml DI water
3. Add 1ml of 30 % H_2O_2
4. Place the rack of tubes into a hot water bath at 85-90 °C for 20 minutes
5. Add 10ml of conc. HCl (12.1 M)
6. Place rack back in water bath for 20 minutes
7. Remove and let stand for 12 hours

The same soil extracts are run twice

- One with acid treatment
- Other without acid treatment

For other cations and anions except selenium and arsenic, the extracts are run without treatment.

Digestion with Aqua Regia and Hydrofluoric Acid in a Closed Vessel (Hossner, 1996)

Apparatus:

1. Wide mouth polypropylene bottle (250ml) with screw cap
2. Bottle Shaker
3. Electric Hot Plate
4. 250ml beaker (for filtering extract)
5. Plastic pipette
6. Teflon tape
7. Glass bottles (250ml)

Reagents:

1. Aqua regia {3ml of 12 M (36%) HCl + 1 ml of 15 M HNO_3(70)}
2. Hydrofluoric acid, 29 M (48%)
3. Boric acid (H_3BO_4), saturated solution

Procedures:

1. Place 0.5g soil sample into the polypropylene bottle
2. Add 1ml Aqua regia by pipette
3. Add 10ml HF by plastic pipette
4. Cap the bottle immediately. Double wrap the cap with teflon tape to ensure tightness
5. Shake it on the shaker for 2-8 hours
6. Heat the bottle on a hot plate (75-100°C) for 30 minutes

7. Cool the bottle to room temperature
8. Add 100ml of saturated H_3BO_4 solution and immediately cap the bottle
9. Cool the bottle to room temperature to minimize the above exothermic reaction
10. Dilute the bottle contents with DI water to 200g by placing the bottle on a balance
11. Store the extract after filtering (0.45μ) in glass bottles (250ml)
12. Analyze the extract within 4 weeks

Purpose:

1. To determine total metals by ICP/ASS
2. Total selenium by HGAAS

Acid treatment and sample preparation for selenium analysis by HGAAS:

Digestion and sample preparation:

1. Add 3ml extract into a 50ml test tube
2. Add 12ml DI water
3. Add 1ml of 30 % H_2O_2
4. Place the rack of tubes into a hot water bath at 85-90 °C for 20 minutes
5. Add 10ml of conc. HCl (12.1 M)
6. Place rack back in water bath for 20 minutes
7. Remove and let stand for 12 hours

The same soil sample (extract) will be run twice

- One with acid treatment
- Other without acid treatment

Appendix E:Chemical Data of 2001 Soil Moisture Samples

Chemical data of 2001 Soil Moisture Samples Aug 01, 2001

Sr No	Sample	Depth(m)	Date	X-coord	Y-coord	Cl (ppm)	NO_3- N(ppm)	SO_4^{-2}(ppm)	Cond.(mS/cm)	TOC (ppm)	Hg(ppm)	As(ppb)	Se(ppb)
1	UASW	Shallow	1-Aug-01	301913.75	4922718.71	15.3	BD	515.0	2.57	16.70	0.0022	1.57	1.37
2	MASW	Shallow	1-Aug-01	301870.46	4922692.24	15.2	BD	436.0	2.16	0.60	0.0005	1.49	0.75
3	LASW	Deep	1-Aug-01	301832.30	4922660.04	276	BD	1820	8.74	58.80	0.0048	1.87	2.85
4	LASW	Shallow	1-Aug-01	301832.30	4922660.04	80.6	1.0	159.0	1.81	24.30	0.0019	2.27	1.53
5	1WESD	Deep	1-Aug-01	297104.68	4924134.34	18.5	9.3	45.10	0.94	10.00	0.0004	0.48	0.36
6	1WESD	Shallow	1-Aug-01	297104.68	4924134.34	18.3	5.7	44.10	0.85	6.80	0.0039	0.48	0.41
7	2WESD	Shallow	1-Aug-01	297269.08	4924127.36	9.3	13.2	19.10	0.79	8.50	0.0006	1.11	0.56
8	3WESD	Deep	1-Aug-01	297443.41	4924140.47	28.5	1.2	41.00	1.00	11.30	0.0003	2.58	0.92
9	3WESD	Shallow	1-Aug-01	297443.41	4924140.47	38.4	1.0	56.30	0.95	12.70	0.0004	1.53	0.83
10	4WESD	Shallow	1-Aug-01	297632.83	4924127.16	18.8	1.0	94.80	1.28	17.70	0.0001	1.67	1.34
11	5WESD	Deep	1-Aug-01	297427.32	4924050.16	145	1.6	301.0	2.29	10.50	0.0010	1.68	0.78
12	5WESD	Shallow	1-Aug-01	297427.32	4924050.16	58.2	1.0	221.0	1.89	22.90	0.0010	1.93	1.14

Chemical data of 2001 Soil Moisture Samples Aug 09, 2001

Sr No	Sample	Depth(m)	Date	X-coord	Y-coord	Cl(ppm)	NO3 - N(ppm)	$SO4^{-2}$(ppm)	Cond(mS/cm)	TOC(ppm)	As(ppb)	Hg(ppm)	Se(ppb)
1	UASW	Shallow	9-Aug-01	301913.75	4922718.71	4.3	BD	533.0	2.55	13.70	1.25	0.0004	1.17
2	MASW	Shallow	9-Aug-01	301870.46	4922692.24	17.9	BD	432.0	2.23	6.50	0.97	0.0007	0.63
4	LASW	Shallow	9-Aug-01	301832.30	4922660.04	75.2	BD	143.0	1.77	18.10	2.06	0.0017	2.19
5	1WESD	Deep	9-Aug-01	297104.68	4924134.34	18.2	14.3	30.30	0.91	11.60	0.38	0.0017	0.36
6	1WESD	Shallow	9-Aug-01	297104.68	4924134.34	9.2	4.0	17.20	0.74	14.20	0.39	0.0263	0.37
7	2WESD	Shallow	9-Aug-01	297269.08	4924127.36	1.0	16.5	8.40	0.75	4.90	0.94	0.0068	0.60
8	3WESD	Deep	9-Aug-01	297443.41	4924140.47	17.8	1.00	22.60	0.92	11.20	1.78	0.0011	0.79
9	3WESD	Shallow	9-Aug-01	297443.41	4924140.47	13.3	1.00	18.10	0.79	1.00	0.80	0.0048	0.67
10	4WESD	Shallow	9-Aug-01	297632.83	4924127.16	8.0	1.00	85.80	1.34	26.50	1.05	0.0071	1.43
11	5WESD	Deep	9-Aug-01	297427.32	4924050.16	133	1.00	409.0	2.78	25.00	1.19	0.0017	1.13
12	5WESD	Shallow	9-Aug-01	297427.32	4924050.16	48.2	1.00	242.0	2.02	36.80	0.89	0.0055	1.25

Chemical data of 2001 Soil Moisture Samples Aug 27, 2001

Sr No	Sample	Depth(m)	Date	X-coord	Y-coord	Cl(ppm)	NO3 - N(ppm)	$SO4^{-2}$(ppm)	Cond(mS/cm)	TOC(ppm)	As(ppb)	Hg(ppm)	Se(ppb)
10	4WESD	Shallow	27-Aug-01	297632.83	4924127.16	9.9	BD	315.0	1.44	12.60	1.59	BD	1.34
9	3WESD	Shallow	27-Aug-01	297443.41	4924140.47	12.0	BD	39.80	0.84	3.90	1.30	BD	0.59
8	3WESD	Deep	27-Aug-01	297443.41	4924140.47	22.6	BD	69.80	1.06	BD	2.66	BD	0.72
7	2WESD	Shallow	27-Aug-01	297269.08	4924127.36	3.4	15.90	31.40	0.83	1.00	1.34	0.0015	0.56
6	1WESD	Shallow	27-Aug-01	297104.68	4924134.34	8.1	6.60	40.20	0.76	5.30	0.52	0.0122	0.36
5	1WESD	Deep	27-Aug-01	297104.68	4924134.34	12.8	16.20	40.90	0.93	3.50	0.38	BD	0.31
2	MASW	Shallow	27-Aug-01	301870.46	4922692.24	28.2	BD	1280	2.27	3.90	BD	BD	0.63

APPENDIX F: Chemical Analysis Data of 2002 Water Samples

Sr. No	Sample	Date	X_coord	Y-coord	Temp (C)	Cond(µs/cm)	pH	DO(mg/L)	Cl⁻(mg/L)	NO_3^--N(mg/L)	$SO4^{-2}$(mg/L)	PO_4^{3-}(mg/L)	P(mg/L)	TC(mg/L)	IC(mg/L)
1	P1	21-Aug-02	301798.88	4922918.78	23.30	5770	7.50	4.60	76.80	21.0	7243	BD	0.04	60.1	18
2	P2	21-Aug-02	301978.13	4922264.03	22.00	1670	6.90	5.80	19.77	21.0	1628	BD	0.04	54.2	34
3	P3	22-Aug-02	302358.45	4924633.95	20.30	1163	6.80	5.60	23.89	21.0	1070	BD	0.00	29.2	12
4	S1	22-Aug-02	301204.35	4924371.15	18.30	10190	7.80	2.70	495.0	165.2	8608	BD	BD	123.5	101
5	ASTRA	22-Aug-02	301871.39	4922814.28	17.80	5900	7.80	2.60	42.61	26.1	6543	BD	BD	186.7	162
6	RANCH	22-Aug-02	297146.00	4924670.00	23.00	2570	7.80	5.10	48.50	21.0	2538	0.26	BD	102.9	93
7	P4	22-Aug-02	297522.82	4924085.54	23.10	4530	6.70	4.30	64.78	29.0	5830	BD	BD	112.2	108.7

Sr. No	Sample	Mg^{++}(mg/L)	Na^+(mg/L)	K^+(mg/L)	Fe(mg/L)	Mn^{++}(mg/L)	S(mg/L)	Cu(mg/L)	Mo(mg/L)	Zn(mg/L)	Se*(µg/L)	Se**(µg/L)	HCO_3^-(mg/L)	TOC(mg/L)	Ca^{++}(mg/L)
1	P1	902.2	317.0	34.16	0.06	0.04	2109	0.07	0.04	BD	6.22	8.03	89.16	42.65	576.8
2	P2	137.9	183.4	18.96	0.05	0.02	447.5	BD	0.00	BD	1.17	2.44	171.4	20.46	133.9
3	P3	87.63	132.4	20.44	0.01	0.00	274.8	BD	0.04	BD	1.98	2.40	60.96	17.18	231.4
4	S1	900.3	428.4	31.96	0.02	0.01	2331	BD	BD	0.01	4179	1740	515.1	22.10	1010
5	ASTRA	427.0	253.3	17.23	0.02	55.0	1446	0.08	0.01	0.06	10.76	2.59	824.0	24.50	1039
6	RANCH	233.1	102.8	21.63	0.06	0.11	673.0	0.01	0.02	0.00	21.15	1.70	472.6	9.88	712.8
7	P4	108.3	250.6	11.98	0.07	0.20	1203	0.03	0.04	0.00	6.51	2.20	552.2	3.50	646.2

Note: Se** is Se analysis results from HGAAS
Se* is Se analysis results from GFAAS
BD : below Detection Limit

Appendix G (A) : Chemical analysis data of 2001 Soil Samples (hot water extraction)

Sr. No	Sample	Elevation(m)	X_coord	Y_coord	Depth(m)	Se(ppb)	As(ppb)	Ca(ppm)	Cu(ppm)	Fe(ppm)	Mg(ppm)	Mn(ppm)	Mo(ppm)	Na(ppm)	P(ppm)	Zn(ppm)
1	1WESD	2119	297104.68	4924134.34	0.56	0.63	10.89	110.3	0.05	7.04	8.11	0.02	0.02	7.11	1.00	0.08
2	1WESD	2119	297104.68	4924134.34	0.94	0.81	12.56	83.47	0.30	10.90	10.10	0.04	0.08	32.14	1.05	0.16
3	2WESD	2064	297269.08	4924127.36	0.56	0.88	18.85	123.3	0.06	14.41	9.11	0.05	0.09	53.42	4.32	0.14
4	2WESD	2064	297269.08	4924127.36	1.07	0.23	2.80	2878	----	0.40	154.7	0.03	0.05	612.0	0.37	0.17
5	3WESD	2028	297443.41	4924140.47	0.56	1.10	26.11	111.2	0.08	23.84	11.34	0.08	0.14	54.16	1.51	0.14
6	3WESD	2028	297443.41	4924140.47	1.12	4.01	123.02	91.52	0.21	184.6	47.91	0.55	0.32	216.0	3.66	0.59
7	4WESD	2014	297632.83	4924127.16	0.56	1.08	7.90	168.7	0.10	7.58	10.87	0.03	0.16	99.34	1.14	0.08
8	4WESD	2014	297632.83	4924127.16	1.07	0.93	19.32	124.2	0.09	14.55	7.59	0.07	0.21	84.37	1.11	0.09
9	5WESD	2043	297[illegible]7.32	4924050.16	0.56	0.71	19.26	188.9	0.19	8.30	15.57	0.06	0.32	93.34	5.69	0.13
10	5WESD	2043	297427.32	4924050.16	1.14	0.72	4.81	279.9	0.06	0.68	18.11	0.02	0.17	152.4	0.64	0.05
11	UASW	2250	301913.75	4922718.71	0.56	0.49	1.97	2970	----	----	208.7	0.02	0.92	115.6	BD	0.12
12	UASW	2250	301913.75	4922718.71	1.12	12.76	2.95	2108	----	----	389.3	0.02	0.29	2423	BD	0.11
13	MASW	2225	301870.46	4922692.24	0.56	0.20	2.48	2667	----	----	58.86	0.01	0.97	37.43	BD	0.14
14	MASW	2225	301870.46	4922692.24	1.07	2.63	2.45	2874	----	----	700.4	0.01	0.54	705.2	BD	0.17
15	LASW	2210	301832.30	4922660.04	0.51	50.99	104.14	64.45	0.35	165.0	49.34	0.33	1.13	781.8	3.12	0.51
16	LASW	2210	301832.30	4922660.04	0.97	17.47	1.99	2313	0.05	0.16	365.2	0.01	0.28	3279	BD	0.16
17	1A	2302	300989.48	4923061.91	0.30	0.50	23.53	133.9	0.15	19.69	4.15	0.04	0.19	17.25	0.35	0.17
18	2A	2295	301039.64	4923095.59	0.30	0.94	19.31	105.9	0.12	13.52	17.46	0.04	0.14	67.33	0.48	0.08
19	3A	2272	301096.54	4923132.77	0.30	0.49	15.11	144.4	0.18	8.10	11.64	0.04	0.12	23.36	0.06	0.07
20	4A	2274	301148.13	4923170.10	0.30	16.29	69.59	92.60	0.19	84.70	27.13	0.24	0.38	277.7	1.31	0.30
21	5A	2254	301200.94	4923203.70	0.30	12.58	61.34	100.9	0.20	87.17	27.91	0.24	0.38	283.9	2.45	0.31
22	6A	2237	301255.13	4923239.10	0.30	8.12	71.45	121.6	0.18	62.35	21.09	0.25	0.14	188.7	1.50	0.22
23	7A	2230	301307.99	4923274.55	0.30	6.69	136.92	104.6	0.35	182.9	66.79	0.71	0.34	394.5	3.70	0.59
24	8A	2230	301358.19	4923310.08	0.30	1.49	29.77	106.0	0.15	19.02	15.69	0.07	0.45	146.2	0.61	0.12
25	9A	2222	301383.91	4923325.97	0.30	0.49	4.06	3271	0.03	0.24	19.90	0.02	2.24	50.36	0.58	0.22
26	10AA	2177	301395.48	4923357.12	0.30	1.09	3.21	2307	0.01	----	189.3	0.18	0.04	893.2	BD	0.20
27	11AA	2186	301400.50	4923347.70	0.30	5.80	10.21	343.7	0.01	0.10	31.57	0.09	0.09	1685	BD	0.06
28	12B	2227	301383.54	4923183.30	0.30	6.98	2.62	4565	0.09	----	7.50	0.04	0.65	13.91	0.00	0.17
29	13B	2224	301364.52	4923169.06	0.30	36.41	5.08	3123	0.05	----	35.03	0.08	0.71	51.42	2.24	0.16
30	14B	2218	301343.83	4923143.75	0.30	27.49	28.54	158.7	0.10	19.58	9.10	0.06	0.50	108.5	1.48	0.12
31	15B	2246	301319.33	4923124.11	0.30	5.32	41.45	92.25	0.19	48.84	21.23	0.14	0.11	117.0	1.44	0.23

Note: For all the samples K was BD

Appendix G(B) : Chemical analysis data of 2001 Soil Samples (hot water extraction)

Sr No	Sample	Elevation(m)	X_coord	Y_coord	Depth(m)	Se(ppb)	As(ppb)	Ca(ppm)	Cu(ppm)	Fe(ppm)	Mg(ppm)	Mn(ppm)	Mo(ppm)	Na(ppm)	P(ppm)	Zn(ppm)
32	16B	2252	301298.64	4923098.80	0.30	5.51	58.53	119.2	0.26	113.6	40.20	0.29	0.18	227.2	2.94	0.39
33	17B	2249	301286.08	4923078.80	0.30	36.50	116.16	120.4	0.43	135.1	45.25	0.50	0.99	471.1	4.79	0.48
34	18C	2311	301448.27	4922432.71	0.30	7.03	102.61	114.0	0.31	66.56	22.76	0.19	0.41	411.6	2.21	0.24
35	19C	2292	301492.84	4922457.29	0.30	5.09	36.69	148.3	0.16	41.53	4.50	0.06	0.04	61.6	2.59	0.28
36	20C	2278	301555.00	4922492.46	0.30	54.91	5.62	2406	0.10	0.50	617.2	0.03	0.56	7228	0.00	0.15
37	21C	2283	301607.58	4922518.65	0.30	7.67	22.75	120.5	0.12	30.84	13.15	0.06	----	106.0	4.41	0.17
38	22C	2273	301659.12	4922554.14	0.30	4.79	18.70	146.4	0.11	11.83	2.15	0.03	0.22	15.07	1.92	0.09
39	23C	2254	301713.25	4922587.70	0.30	4.84	53.37	93.69	0.17	34.57	14.07	0.14	----	142.53	1.33	0.16
40	24C	2255	301738.91	4922601.74	0.30	15.98	28.99	100.5	0.12	19.57	11.54	0.07	0.27	225.1	0.99	0.10
41	25C	2252	301763.35	4922619.53	0.30	8.10	12.39	106.3	0.06	11.79	8.70	0.14	0.18	16.60	0.45	0.04
42	26C	2216	301790.28	4922631.67	0.30	11.67	22.72	216.9	0.18	16.15	7.61	0.10	0.13	264.3	0.35	0.09
43	27C	2254	301943.22	4922727.08	0.30	16.15	19.59	151.2	0.11	9.62	6.11	0.12	0.22	60.67	0.44	0.04
44	28C	2258	301970.20	4922741.09	0.30	34.36	132.74	134.6	0.38	255.1	77.80	1.02	0.25	605.9	3.81	0.82
45	29C	2261	301995.91	4922756.99	0.30	6.00	15.54	112.6	0.07	10.21	12.95	0.09	----	92.20	0.00	0.05
46	30C	2269	302018.91	4922771.11	0.30	6.51	56.07	75.28	0.16	42.99	21.58	0.25	0.06	290.4	1.56	0.15
47	31C	2258	302071.55	4922799.16	0.30	38.77	127.95	124.1	0.25	94.49	37.54	0.36	0.51	552.1	3.93	0.33
48	32C	2261	302124.24	4922829.05	0.30	4.95	57.39	90.23	0.22	49.95	25.74	0.32	0.07	218.0	1.59	0.21
49	33C	2278	302181.08	4922864.38	0.30	7.00	96.23	83.34	0.33	123.5	47.25	0.58	0.16	358.1	3.33	0.74
50	34C	2255	302230.89	4922886.96	0.30	15.63	103.80	92.88	0.30	197.7	69.34	0.59	0.17	273.2	4.70	0.64
51	35C	2253	302289.00	4922920.41	0.30	5.43	81.75	129.8	0.26	132.3	42.93	0.40	0.09	210.2	3.08	0.44
52	36C	2263	302342.90	4922946.56	0.30	5.36	40.09	99.97	0.18	42.44	17.45	0.10	0.06	139.1	1.90	0.16
53	37C	2265	302399.52	4922974.49	0.30	21.36	58.97	84.79	0.28	105.8	41.37	0.49	0.08	95.00	5.24	0.37
54	38C	2267	302487.15	4923018.15	0.30	14.38	32.64	102.8	0.19	37.74	19.32	0.14	0.07	109.3	2.81	0.14
55	39C	2267	302537.29	4923051.84	0.30	8.58	72.41	83.97	0.27	296.9	93.38	0.89	0.05	56.17	4.89	0.91
56	40D	2244	302013.56	4922682.32	0.30	17.02	2.69	3326	0.07	0.47	31.53	0.01	0.66	25.70	0.00	0.11
57	41D	2241	302057.62	4922690.25	0.30	6.52	18.03	87.09	0.04	9.77	8.46	0.02	0.24	10.60	3.72	0.04
58	42D	2246	302106.53	4922683.20	0.30	12.44	25.91	85.21	0.07	12.86	11.78	0.01	0.80	17.65	0.00	0.10
59	43ED	2035	297356.96	4924135.74	0.30	21.62	123.08	147.3	0.43	331.7	109.4	0.90	0.27	419.4	9.49	0.90
60	44ES	2035	297356.96	4924135.74	0.30	7.02	54.09	151.9	0.27	81.54	27.42	0.52	0.12	107.2	3.54	0.30
61	45ED	2075	297185.52	4924129.96	0.30	6.76	26.54	132.0	0.12	24.02	7.08	0.08	0.13	37.97	2.07	0.10
62	46ES	2075	297185.52	4924129.96	0.30	6.71	17.69	130.9	0.08	10.91	7.84	0.03	0.02	14.84	0.36	0.04
63	SHALE	2217	301768.82	4922799.10	0.30	29.51	3.67	3560	0.59	0.11	258.3	0.08	0.03	2291	0.00	0.15

Appendix H : Chemical analysis data of 2001 Soil Samples (acid digested)

Sr.No	Sample	Elevation(m)	X_coord	Y_coord	Ca(ppm)	Cu(ppm)	Fe(ppm)	K(ppm)	Mg(ppm)	Mn(ppm)	Mo(ppm)	Na(ppm)	P(ppm)	S ppm)	Zn(ppm)	Se(ppm)	As(ppm)
1	4A	2274	301148.13	4923170.10	35368	199.79	87902	20340	28870	6807	4.23	1217	526.46	804	29.43	1.22	13.13
2	5A	2254	301200.94	4923203.70	43885	175.85	84855	19117	25380	7533	8.62	1440	525.48	951	28.76	1.02	12.88
3	7A	2230	301307.99	4923274.55	38294	191.10	82829	20066	25455	8045	8.01	1662	559.53	808	28.91	1.12	12.67
4	13B	2224	301364.52	4923169.06	82414	183.95	85145	18183	27081	6720	11.38	1131	535.97	18719	30.01	3.29	13.25
5	14B	2218	301343.83	4923143.75	53169	165.41	88046	18875	24347	7953	3.28	1142	587.07	1223	29.53	1.93	12.90
6	16B	2252	301298.64	4923098.80	52766	203.66	88415	8619	26287	8082	5.58	1421	606.32	1040	31.07	1.16	12.79
7	17B	2249	301286.08	4923078.80	40434	252.18	92395	8619	26287	7404	10.76	1328	378.29	1141	34.64	1.44	13.45
8	20C	2278	301555.00	4922492.46	98172	252.18	85987	21168	27748	3535	9.29	2681	386.66	36622	35.69	10.24	10.33
9	24C	2255	301738.91	4922601.74	71164	152.59	85895	16024	31245	6199	8.51	1246	638.42	1193	27.18	1.10	9.84
10	25C	2252	301763.35	4922619.53	388819	10.09	83473	16024	23130	31573	8.23	1252	231.44	2357	21.08	2.46	10.00
11	28C	2258	301970.20	4922741.09	73377	231.26	99895	20315	27278	8487	8.19	1665	700.05	1202	32.91	3.49	15.36
12	30C	2269	302018.91	4922771.11	103287	125.77	78618	15530	24690	10646	1.41	1000	574.04	1070	24.95	0.53	9.40
13	31C	2258	302071.55	4922799.16	52783	218.09	82950	18865	23308	13110	1.41	1611	559.29	994	32.99	1.24	12.28
14	34C	2255	302230.89	4922886.96	27049	166.56	83377	20869	24435	9197	1.91	1186	465.35	516	27.60	0.64	12.13
15	35C	2253	302289.00	4922920.41	74835	166.12	77532	18195	23860	7302	4.46	913	463.70	887	28.04	0.97	11.75
16	37C	2265	302399.52	4922974.49	18101	135.97	82149	19916	24202	9429	1.88	1286	493.02	748	26.98	0.71	12.33
17	39C	2267	302537.29	4923051.84	15086	150.13	84741	21518	21847	8674	1.88	1012	568.84	675	27.88	0.74	11.88
18	40D	2244	302013.56	4922682.32	55439	238.07	89382	20990	20919	3369	18.33	649	388.86	20029	32.19	3.31	11.52
19	42D	2246	302106.53	4922683.20	55530	209.02	85722	12728	29531	5767	24.80	554	483.48	567	40.25	2.40	19.06
20	43ED	2035	297356.96	4924135.74	33355	161.87	91798	22733	21717	9301	0.94	1753	637.60	578	32.76	0.76	11.28
21	44ES	2035	297356.96	4924135.74	34165	137.17	92899	22497	27436	8401	0.10	1879	590.96	508	32.12	0.84	12.19
22	46ES	2075	297185.52	4924139.96	39449	139.59	93528	21887	28842	8138	0.10	1692	612.65	541	31.64	1.02	12.43

Note: All samples are collected at 0.30 m depth from the surface

Appendix : I (A) : Chemical data of 2002 Soil Samples (saturated paste extraction)

Sr No	Sample	Date	X_coord	Y_coord	Depth	Se*(ppb)	Se**(ppb)	Se***(ppb)	SeTotal (ppm)	As(ppm)	OC%	IC%	Cl(ppm)	$SO4^{-2}$(ppm)
1	SBSH	21-Aug-02	297522.82	4924085.54	0.30	9.58	16.18	0.00	1.74	11.16	ND	ND	50.39	5983.72
2	ASNW-A	21-Aug-02	301871.39	4922814.28	1.50	14.88	19.26	0.00	2.68	15.28	1.56	8.12	77.28	6497.85
3	ASNW-B	21-Aug-02	301871.39	4922814.28	2.00	42.11	42.89	0.00	2.84	15.19	1.49	5.01	41.89	6793.27
4	ASNW-C	21-Aug-02	301871.39	4922814.28	2.50	22.13	23.30	0.00	4.20	17.97	1.79	10.78	32.35	7085.92
5	ASNW-D	21-Aug-02	301871.39	4922814.28	3.00	74.97	71.84	5.28	6.41	19.15	2.13	11.63	19.28	6278.25
6	ASNW-E	21-Aug-02	301871.39	4922814.28	3.50	89.28	76.48	0.89	3.81	15.30	1.67	9.83	48.63	6601.29
7	ASNW-F	21-Aug-02	301871.39	4922814.28	1.00	78.97	69.10	1.61	2.52	16.17	0.94	11.26	168.72	6505.89
8	TNE-1	21-Aug-02	301956.40	4922780.56	0.50	5.12	9.95	0.74	2.92	12.53	ND	ND	18.52	3319.68
9	TNE-2	21-Aug-02	301956.40	4922780.56	1.00	28.58	44.47	0.98	2.68	16.53	ND	ND	27.57	4059.07
10	T3N-1	21-Aug-02	301902.04	4922722.18	0.50	15.18	7.78	0.82	2.78	18.32	ND	ND	31.82	195.71
11	T3N-2	21-Aug-02	301902.04	4922722.18	1.00	17.91	24.36	1.03	2.52	16.13	ND	ND	28.80	4754.32
12	T3M-1	21-Aug-02	301901.82	4922688.83	0.50	1.70	6.15	0.76	5.63	21.70	ND	ND	26.48	3293.59
13	T3M-2	21-Aug-02	301901.82	4922688.83	1.00	1.30	7.57	0.79	1.65	16.74	ND	ND	14.71	4500.12
14	T3S-1	21-Aug-02	301944.36	4922673.09	0.50	28.86	16.19	1.05	6.23	27.22	ND	ND	26.10	114.80
15	T3S-2	21-Aug-02	301944.36	4922673.09	1.00	47.83	75.14	0.95	5.05	22.55	ND	ND	20.80	5544.65
16	SBA3-1	21-Aug-02	301807.94	4922640.55	0.50	85.42	130.53	2.70	5.06	19.20	ND	ND	52.51	7445.73
17	SBA3-2	21-Aug-02	301807.94	4922640.55	1.00	22.39	26.04	2.84	6.37	18.89	ND	ND	55.05	5272.66
18	SBSH-1	21-Aug-02	301965.30	4922627.98	0.50	142.04	104.68	5.00	5.75	16.77	1.63	15.63	52.89	7544.22
19	SBSH-2	21-Aug-02	301965.30	4922627.98	1.00	30.77	22.83	1.90	3.74	13.31	0.70	3.20	53.07	7001.07
20	P1-A	21-Aug-02	301798.88	4922918.78	0.10	45.84	23.85	1.46	4.05	12.62	1.79	7.90	22.63	1298.28
21	P1-B	21-Aug-02	301798.88	4922918.78	0.50	7.92	11.93	1.66	1.93	14.39	1.22	4.22	59.91	6656.90
22	P2-A	22-Aug-02	301978.13	4922264.03	0.10	12.28	14.27	3.90	0.70	10.94	ND	ND	10.97	3551.55
23	P2-B	22-Aug-02	301978.13	4922264.03	0.50	11.60	14.24	2.95	0.71	14.57	ND	ND	8.30	4563.02
24	P3-A	22-Aug-02	302358.45	4924633.95	0.10	2.72	13.10	5.56	1.40	12.68	ND	ND	20.88	4156.00
25	P3-B	22-Aug-02	302358.45	4924633.95	0.50	8.09	20.97	2.36	1.41	11.31	ND	ND	23.67	4040.54
26	S1-A	22-Aug-02	301204.35	4924371.15	0.10	698.77	415.27	54.34	7.49	10.25	0.60	5.24	212.20	7919.73
27	S1-B	22-Aug-02	301204.35	4924371.15	0.50	683.23	455.66	25.33	5.62	10.78	0.54	4.96	151.01	7700.33
28	P4-A	22-Aug-02	302308.73	4922708.71	0.20	282.11	107.97	0.94	1.62	13.37	0.94	10.57	26.30	503.98
29	P4-B	22-Aug-02	302308.73	4922708.71	0.75	63.79	25.72	1.68	1.81	16.74	1.08	8.14	14.58	812.09
30	P4-C	22-Aug-02	302308.73	4922708.71	1.00	27.41	11.97	1.31	1.43	13.82	0.70	7.90	9.19	1051.58
31	P4-D	22-Aug-02	302308.73	4922708.71	1.50	68.34	34.94	1.42	1.25	15.85	0.54	11.23	12.45	1358.16
32	P4-E	22-Aug-02	302308.73	4922708.71	2.00	21.70	28.27	11.73	1.41	13.67	0.67	9.55	1594.40	8458.89

Note: Se** is Se analysis results from HGAAS

Se* is Se analysis results from GFAAS

Se*** is Se analysis results from HGAAS with little acidification

Appendix: I (B) : Chemical data of 2002 Soil Samples (saturated paste extraction)

Sr. No	Sample	NO_3^--N(ppm)	PO_4^{3-}(ppm)	Ca(ppm)	Cu(ppm)	Fe(ppm)	K(ppm)	Mg(ppm)	Mn(ppm)	Mo(ppm)	Na(ppm)	P(ppm)	S(ppm)	Zn(ppm)
1	SBSH	0.22	BD	1385.20	0.23	0.17	59.40	665.1	130	0.11	151.9	0.15	1731	0.03
2	ASNW-A	0.24	BD	1321.58	0.52	0.04	0.19	328.1	3.89	0.11	265.7	0.28	1854	0.01
3	ASNW-B	0.23	BD	1043.86	0.20	0.02	22.24	222.5	2.36	0.08	255.3	0.09	1652	0.02
4	ASNW-C	BD	BD	1055.67	0.22	0.01	23.99	202.9	6.60	0.12	277.0	0.14	1786	0.01
5	ASNW-D	0.21	BD	1689.11	0.03	0.07	0.05	314.1	4.34	0.06	287.4	0.07	2227	0.00
6	ASNW-E	BD	BD	1218.55	0.05	0.04	37.12	335.2	19.2	0.01	198.6	0.06	1761	0.02
7	ASNW-F	0.37	BD	1089.54	0.56	0.05	21.17	302.6	0.40	0.04	177.6	0.15	1488	0.01
8	TNE-1	0.56	BD	1574.89	0.15	0.00	2.13	19.95	0.34	0.68	15.43	0.05	864.2	0.01
9	TNE-2	0.57	BD	972.21	0.10	0.02	8.76	346.6	0.56	0.18	56.65	0.02	994.4	0.01
10	T3N-1	0.28	BD	176.73	0.21	0.11	1.35	8.04	0.09	0.29	10.55	0.08	51.16	0.00
11	T3N-2	0.29	0.12	1406.73	0.25	0.02	9.40	235.9	0.37	0.13	87.27	0.08	1300	0.04
12	T3M-1	0.35	BD	1541.30	0.35	0.03	7.37	25.81	0.52	0.18	19.63	0.06	901.3	0.03
13	T3M-2	BD	BD	1193.16	0.13	0.12	12.21	399.6	0.20	0.03	20.61	0.04	955.3	0.01
14	T3S-1	0.50	BD	135.38	0.28	0.05	4.57	16.04	0.19	0.84	12.64	0.00	32.19	0.01
15	T3S-2	0.42	BD	1264.73	0.17	0.04	15.24	365.4	0.76	0.26	123.9	0.03	1336	0.02
16	SBA3-1	1.84	BD	509.63	0.02	0.03	0.06	565.0	0.20	0.14	424.0	0.01	2645	0.00
17	SBA3-2	1.04	0.08	900.50	0.30	0.00	16.96	186.2	1.50	0.04	166.3	0.03	1126	0.04
18	SBSH-1	1.04	0.10	1231.21	0.30	0.01	29.52	277.3	0.85	0.08	328.8	0.01	1998	0.03
19	SBSH-2	0.67	0.08	1191.04	0.06	0.00	25.85	286.6	0.65	0.00	258.3	0.01	1731	0.02
20	P1-A	BD	0.12	436.94	0.01	0.06	0.34	58.24	1.73	0.30	66.50	0.06	418.7	0.01
21	P1-B	BD	BD	987.27	0.08	0.05	46.63	425.7	25.1	0.04	175.1	0.13	1463	0.01
22	P2-A	BD	BD	917.77	0.14	0.05	41.89	419.8	5.65	0.23	129.8	0.19	1152	0.00
23	P2-B	BD	BD	1056.59	0.12	0.03	61.88	429.3	15.4	0.02	62.12	0.08	1127	0.02
24	P3-A	BD	BD	1553.89	0.08	0.06	56.65	214.1	38.1	0.00	37.32	0.20	996.6	0.00
25	P3-B	0.23	0.25	1807.38	0.06	0.03	39.86	193.9	38.3	0.64	63.21	0.25	1187	0.01
26	SJ-A	0.57	BD	1398.22	0.38	0.08	4.55	676.3	5.69	0.11	411.0	0.20	2613	0.03
27	SJ-B	2.47	BD	1264.14	0.37	0.06	34.47	579.0	2.56	0.04	344.7	0.10	2307	0.03
28	P4-A	2.40	BD	430.79	0.02	0.08	-0.09	45.22	0.58	0.20	14.51	0.03	170.0	0.00
29	P4-B	0.51	BD	532.02	0.02	0.01	-0.07	44.93	0.56	0.20	13.54	0.08	269.9	0.01
30	P4-C	0.24	BD	607.69	0.15	0.14	-0.31	55.98	1.50	0.10	14.09	0.08	329.9	0.01
31	P4-D	0.26	BD	573.78	0.31	0.03	31.20	59.39	4.48	0.47	39.58	0.13	385.7	0.02
32	P4-E	0.25	BD	1421.13	0.02	0.04	0.03	1378	3.95	0.20	436.2	0.05	3748	0.00

Appendix J : Chemical analysis data of 2002 Soil Samples (acid digested)

Sr.No	Sample ID	Date	X_coord	Y_coord	Depth	Ca(ppm)	Cu(ppm)	Fe(ppm)	K(ppm)	Mg(ppm)	Mn(ppm)	Mo(ppm)	Na(ppm)	P(ppm)	S ppm)	Zn(ppm)	Se(ppm)	As(ppm)
1	SBSH	21-Aug-02	297522.82	4924085.54	0.30	62964	181.82	89232	22551	30312	14752	4.96	1935	737.9	7222	34.75	1.74	11.16
2	ASNW-A	21-Aug-02	301871.39	4922814.28	1.50	91648	208.41	87822	19087	25147	9086	15.78	1753	688.0	17179	32.02	2.68	15.28
3	ASNW-B	21-Aug-02	301871.39	4922814.28	2.00	57328	232.26	92238	21344	27705	7664	10.85	2218	768.6	4421	34.69	2.84	15.19
4	ASNW-C	21-Aug-02	301871.39	4922814.28	2.50	81405	260.30	98084	21328	26739	10418	13.39	1538	796.6	6989	36.59	4.20	17.97
5	ASNW-D	21-Aug-02	301871.39	4922814.28	3.00	81867	266.09	97040	20907	25977	8571	10.55	1593	692.3	9941	37.86	6.41	19.15
6	ASNW-E	21-Aug-02	301871.39	4922814.28	3.50	48264	198.52	93803	23724	31100	6755	6.41	2267	688.5	10962	33.88	3.81	15.30
7	ASNW-F	21-Aug-02	301871.39	4922814.28	1.00	70818	226.34	87388	19903	24769	8290	13.04	1207	735.1	6061	32.85	2.52	16.17
8	TNE-A	21-Aug-02	301956.40	4922780.56	0.50	283005	281.32	59180	11593	13673	4329	41.46	1211	559.0	56572	29.28	2.92	12.53
9	TNE-2	21-Aug-02	301956.40	4922780.56	1.00	92820	386.89	82981	17155	23321	4818	24.12	1145	546.3	8601	37.47	2.68	16.53
10	T3N-1	21-Aug-02	301902.04	4922722.18	0.50	96628	300.59	91185	18411	22466	4586	30.69	1364	664.5	1274	39.22	2.78	18.32
11	T3N-2	21-Aug-02	301902.04	4922722.18	1.00	92343	298.21	91217	18028	24472	5390	2.81	1082	713.9	10123	36.79	2.52	16.13
12	T3M-1	21-Aug-02	301901.82	4922688.83	0.50	187054	331.28	98060	15696	18344	6146	70.96	1053	809.9	16231	49.26	5.63	21.70
13	T3M-2	21-Aug-02	301901.82	4922688.83	1.00	70802	274.55	109377	19759	26102	5485	19.70	897	858.5	17172	41.82	1.65	16.74
14	T3S-1	21-Aug-02	301944.36	4922673.09	0.50	145741	449.20	123517	18982	22216	5810	54.96	824	948.3	794	57.46	6.23	27.22
15	T3S-2	21-Aug-02	301944.36	4922673.09	1.00	73594	654.78	120876	22173	25375	4560	15.18	1126	876.7	4470	58.00	5.05	22.55
16	SBA3-1	21-Aug-02	301807.94	4922640.55	0.50	120329	270.24	105415	19291	28520	9402	18.62	1720	1106	8100	40.55	5.06	19.20
17	SBA3-2	21-Aug-02	301807.94	4922640.55	1.00	146665	248.99	110334	19896	28008	18588	30.48	1063	1256	8763	41.55	6.37	18.89
18	SBSH-1	21-Aug-02	301965.30	4922627.98	0.50	174247	234.47	100411	17799	27162	21470	13.05	1189	1001	4507	38.23	5.75	16.77
19	SBSH-2	21-Aug-02	301965.30	4922627.98	1.00	27448	131.49	96562	24550	27376	5140	10.70	2438	803.2	4981	34.12	3.74	13.31
20	P1-A	21-Aug-02	301798.88	4922918.78	0.00	53899	195.48	94159	21667	30150	5443	7.70	1917	860.8	6624	36.42	4 05	12.62
21	P1-B	21-Aug-02	301798.88	4922918.78	0.50	45981	175.93	91103	20353	26158	6312	4.99	1320	838.3	3052	35.69	1.93	14.39
22	P2-A	22-Aug-02	301978.13	4922264.03	0.00	45981	175.93	91103	20353	29200	6312	27.04	1584	9.89	1662	35.69	0.70	10.94
23	P2-B	22-Aug-02	301978.13	4922264.03	0.50	45981	175.93	91103	19420	29200	6312	2.55	1248	58.79	587	35.69	0.71	14.57
24	P3-A	22-Aug-02	302358.45	4924633.95	0.00	45981	175.93	92011	19420	29200	6312	2.55	1034	58.79	680	35.69	1.40	12.68
25	P3-B	22-Aug-02	302358.45	4924633.95	0.50	45981	175.93	92011	19420	29200	7662	0.57	1034	782.9	509	37.48	1.41	11.31
26	S1-A	22-Aug-02	301204.35	4924371.15	0.00	69063	121.53	106532	21957	83342	10707	17.67	1958	789.2	5099	39.71	7.49	10.25
27	S1-B	22-Aug-02	301204.35	4924371.15	0.50	70812	113.57	108797	21092	32239	9156	17.67	2009	882.0	7017	41.08	5.62	10.78
28	P4-A	22-Aug-02	302308.73	4922708.71	0.20	34894	208.94	119256	20178	33620	9565	2.14	1091	852.8	765	49.44	1.62	13.37
29	P4-B	22-Aug-02	302308.73	4922708.71	0.75	44018	24.69	115032	18522	26854	9712	2.14	970	848.0	1126	45.45	1.81	16.74
30	P4-C	22-Aug-02	302308.73	4922708.71	1.00	53958	200.02	111253	18522	24254	10563	27.27	1050	797.3	1137	46.71	1.43	13.82
31	P4-D	22-Aug-02	302308.73	4922708.71	1.50	33675	189.62	109828	18658	24966	8832	2.88	1137	910.5	1038	46.23	1.25	15.85
32	P4-E	22-Aug-02	302308.73	4922708.71	2.00	58833	187.45	112928	17191	23640	15997	7.69	1359	805.2	1018	44.82	1.41	13.67

APPENDIX K: Quality Control and Precision

1. QC Run for known Samples for Anions (Ion Chromatography) and Organic Carbon (Shimadzo TOC Analyzer)

QC 1	Cl	Sulfate	Nitrate-N	Phosphate	IC	OC
Expected	40	80	20	20	40	10
Analyzed	41.25	76.22	18.26	18.91	40.43	9.37
	41.64	72.53	19.43	19.22	40.39	9.25
	39.44	75.88	19.23	21.15	40.46	9.29
	42.73	75.12	21.73	20.69	40.40	9.26
	41.26	74.28	21.56	18.69	39.60	9.47
	41.66	77.81	19.29	17.25	39.57	9.43
	37.25	74.89	19.66	21.89	39.89	9.37
	39.22	81.26	22.56	22.68	40.54	9.36
	40.58	81.36	19.55	19.29	40.26	9.34
	40.503	73.58	19.26	18.36	40.68	9.27

QC 1		Mean (ppm)	Std. Dev	Std. Error	Maximum	Minimum	% Error	No of Run	D.L.(ppm)
Chloride	known	40.5	1.58	0.50	42.73	37.25	3.9	10	<2.0
Sulfate	known	76.63	3.07	0.97	81.36	73.58	4.0	10	<2.0
Nitrate-N	known	20.04	1.31	0.41	22.56	18.26	6.5	10	<0.1
Phosphate	known	19.83	1.62	0.51	22.68	18.36	8.2	10	<2.0
IC	known	40.2	0.38	0.12	40.68	39.57	0.9	5	<0.1
OC	known	9.4	0.21	0.07	9.47	9.25	2.2	5	<0.1

After every 10 analyses, two known standards were run to ensure accuracy.

If the error limit exceeds 5%, the standard curve was calibrated again

For every sample batch of 10, there was a duplicate (same sample twice) to recognize homogenization of samples

2. QC Run for known Samples for TOC and Organic Carbon (Shimadzo TOC Analyzer) for soil sample

QC 2	TOC
Expected	10
Analyzed	10.38
	9.55
	9.44
	9.64
	9.20
	9.94
	9.36
	9.18
	9.43
	9.11

QC 2		Mean	Std. Dev	Std. Error	Maximum	Minimum	% Error	No of Run	D.L.(ppm)
TOC	known	9.56	0.39	0.12	10.38	9.11	4.1	10	<2.0

3. Summary of Cations analysis for water and soil extracts (Flame Atomic Absorption Spectrophotometer)

QC 3		Mean	Std. Dev	Std. Error	Maximum	Minimum	% Error	No of Run	D.L.(ppm)
Ca	known	0.51	0.02	0.009	0.38	0.58	3.9	5	<0.05
Mg	known	9.94	0.52	0.233	8.67	10.64	5.2	5	<0.1
Na	known	10.4	0.35	0.157	8.92	11.2	3.4	5	<0.02
K	known	21.4	0.87	0.389	17.6	24.3	4.1	5	<0.5
Mn	known	0.5	0.01	0.004	0.37	0.64	2.0	5	<0.001
Fe	known	0.2	0.02	0.009	0.13	0.22	10.0	5	<0.01

4. Cations analysis for water and soil extracts (Atomic Absorption Spectrophotometer)

QC 4	As	Ca	Cu	Fe	K	Mg	Mn	Mo	Na	P	Se	Zn
	ng/ml	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL	ng/ml	µg/mL
Expected	25	280	0.47	9.5	475	52	0.475	0.475	460	460	10	9.5
Analyzed	25.44	281.53	0.47	9.61	482.35	52.81	0.48	0.48	468.83	465.01	9.88	9.47
	25.74	279.45	0.47	9.56	451.20	52.47	0.48	0.47	465.94	462.93	9.96	9.42
	25.48	278.59	0.46	9.60	478.99	52.68	0.48	0.48	462.88	465.54	9.95	9.45
	25.68	280.43	0.47	9.38	465.21	52.41	0.47	0.48	461.84	452.85	9.89	9.25
	25.18	280.37	0.47	9.46	471.18	53.07	0.47	0.48	461.97	458.75	10.00	9.36
	25.14	275.07	0.46	9.37	473.29	52.56	0.47	0.47	454.93	454.80	10.19	9.29
	25.07	275.50	0.46	9.37	477.26	52.38	0.47	0.47	453.09	452.94	10.09	9.28
	24.91	278.21	0.46	9.45	462.19	52.45	0.48	0.47	458.68	452.57	9.84	9.30
	25.04	275.81	0.46	9.43	462.63	52.44	0.47	0.47	458.38	450.96	9.96	9.24
	25.48	275.71	0.46	9.29	469.45	51.64	0.47	0.45	451.62	444.35	9.99	9.11
	25.66	281.88	0.45	9.43	467.51	52.20	0.47	0.46	455.31	449.85	9.91	9.33
	24.99	277.19	0.46	9.39	464.58	51.94	0.47	0.46	462.05	450.95	9.82	9.25
	24.99	278.85	0.46	9.46	464.14	52.36	0.48	0.46	463.35	454.55	9.86	9.29
	25.57	277.23	0.46	9.40	457.77	52.18	0.47	0.47	463.02	452.93	9.77	9.26
	25.75	279.39	0.47	9.60	469.87	52.43	0.48	0.47	473.17	463.53	9.89	9.42
	26.02	279.13	0.47	9.57	481.21	52.42	0.48	0.46	470.86	461.51	10.16	9.40
	25.14	282.32	0.46	9.58	474.29	53.04	0.48	0.48	469.81	460.60	9.94	9.41
	25.14	280.97	0.46	9.54	480.09	52.81	0.48	0.47	463.29	458.06	9.78	9.36
	24.91	279.69	0.46	9.48	479.56	52.26	0.47	0.46	459.93	453.74	9.86	9.32
	25.13	278.00	0.45	9.42	472.39	52.06	0.47	0.47	459.24	451.68	9.81	9.27
	24.96	279.98	0.46	9.45	479.48	52.48	0.48	0.48	462.54	454.24	9.68	9.33
	25.01	279.03	0.46	9.42	476.07	52.23	0.48	0.46	466.45	452.33	10.17	9.30
	24.62	282.47	0.46	9.57	486.82	53.06	0.48	0.46	464.14	458.49	10.45	9.43
	24.90	279.66	0.46	9.54	488.49	52.71	0.47	0.47	463.11	455.44	10.21	9.35
	24.62	278.51	0.46	9.45	465.25	52.59	0.47	0.46	464.94	453.50	10.26	9.32
	25.19	280.99	0.46	9.39	473.67	52.68	0.47	0.47	463.42	451.79	10.31	9.31
	24.99	280.94	0.46	9.43	485.69	52.72	0.47	0.47	456.30	452.17	10.10	9.30
	24.79	276.89	0.45	9.26	455.44	51.86	0.46	0.46	453.18	445.86	9.88	9.17
	24.66	277.03	0.46	9.30	461.40	52.12	0.46	0.46	452.30	447.41	9.99	9.19
	25.15	277.49	0.45	9.29	457.99	52.25	0.47	0.45	454.21	448.60	9.93	9.21

Summary of QC Analysis 4 : (Atomic Absorption Spectrophotometer)

QC 4	Mean	Std. Dev	Std. Error	Maximum	Minimum	% Error	No of Run	D.L.(ppm)
As	25.17	0.35	0.157	26.02	24.62	1.4	30	0.2 ppb
Ca	278.98	2.04	0.912	282.47	275.07	0.7	30	<0.05
Cu	0.46	0.01	0.004	0.47	0.45	2.2	30	<0.005
Fe	9.45	0.1	0.045	9.61	9.26	1.1	30	<0.01
K	471.31	9.64	4.311	488.49	451.2	2.0	30	<0.5
Mg	52.43	0.35	0.157	53.07	51.64	0.7	30	<0.1
Mn	0.47	0	0.000	0.48	0.46	0.0	30	<0.001
Mo	0.47	0.01	0.004	0.48	0.45	2.1	30	<0.02
Na	461.25	5.59	2.500	473.17	451.62	1.2	30	<0.02
P	454.77	5.46	2.442	465.54	444.35	1.2	30	<0.1
Se	9.99	0.18	0.080	10.45	9.68	1.8	30	0.2 ppb
Zn	9.32	0.09	0.040	9.5	9.11	1.0	30	<0.005

Before Real Analysis began, the following QC sample was run for each parameter tested

Soil Blank (No Se added)

Soil Blank (No Se added)

Soil Blank (No Se added)

Soil Blank (No Se added)

Soil Blank (No Se added)

Soil Blank (No Se added)

Soil Blank (No Se added)

Soil Blank (No Se added)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

Soil Standard (Se added, 2mg/kg)

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